Soil and Alpine Landscape Evolution since the Lateglacial and Early/Mid Holocene in Val di Sole (Trentino, Italy)

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To my daughter Noemi

Summary

The Alpine environment is a fascinating open-laboratory for investigating the effects of climate oscillations during the late Pleistocene and early Holocene. The onset of the Holocene (c. 11,500 years ago) was characterised by an abrupt and rapid climate amelioration with increasing warm conditions. These major climatic changes led to fast glacial retreat comparable to the present-day situation of global warming. Studying the response of the landscape to past climatic shifting can help in predicting future scenarios due to the present global change. Glaciers and related glacial/periglacial processes, as well as geomorphological and vegetation changes, have shaped the area and left visible (i.e., moraines) and hidden (i.e., buried soils, charcoal) signatures of their passage, demonstrating the high sensitivity of high mountain regions to climate shifting. The innovative aspect of the present thesis lies in the use of soils as natural archives of landscape modifications driven by natural climate changes and human impact. The application of different dating techniques allows a multi-faceted approach and enables a more precise evaluation, minimizing errors. The present geochronology thesis has the following main aims:

- Investigation of the oldest possible organic matter (OM) fraction in Alpine soils on a siliceous parent material
- Chemical characterization of this fraction
- Comparison of the ^{14}C ages of this OM fraction with Surface Exposure Dating (SED) ages
- Application of numerical and relative dating techniques on the same geomorphological objects
- Dating of charcoal in soils and reconstruction of the vegetation history
- Reconstruction of the high-Alpine landscape evolution based on selected datable objects

The aim is to reconstruct a chronology of events in an Alpine valley in northern Italy from the Last Glacial Maximum (LGM, ca. 20,000 years ago) to the Holocene period. Detected signals of landscape evolution have been related to the climate and glacier oscillations during the last 18,000–20,000 years and to the human impact occurred since the Neolithic time period. The starting point was the development of a method for the chemical extraction of the resilient pool of the Soil Organic Matter (SOM), followed by radiocarbon dating. The residues at the end of the treatment were aliphatic- and N-enriched and the oldest were dated back to the first deglaciation period, around 17,000 calibrated years ago. These organic residues represent part of the first organic matter (OM) formed after the glacier retreat and their ages to provide a starting time for soil evolution. Crucial information was obtained on the composition of the oldest OM pool and on the main stabilization mechanisms operating in Alpine soils. The formation of soil features like secondary

clay minerals and hydrous oxides of Fe and Al could be directly related to the age of the soil and/or to precise events happened during soil development (i.e., slope processes). The extent of former glaciers at the site has been investigated using cosmogenic nuclides (^{10}Be – Surface Exposure Dating – SED) built up in the surface of boulders deposited by the glaciers in their present position. The combination of SED with the ^{14}C dating of soil resilient organic matter has provided comparable and significant results and helped to explain the glacier oscillations and periglacial activities of the investigated area between 17,000 and 9000 years ago. The age of the soils directly relates to the warm phases of the reference Lateglacial chronology, allowing the estimate of the duration of the individual warm and cold phases in the investigated area. The identification and radiocarbon dating of charcoal fragments have enhanced the chronological investigation of the site. The age of the charcoal fragments was used as a time proxy for soil pedogenesis (in case of an undisturbed soil evolution) and to study the fire and vegetation history of the site. The fire history has revealed 13 fire events in the last 10,000 years and a possible human influence on 7-8 of them during the last 6000 years. Due to climatic and human influences, coniferous species like *Pinus sylvestris* and *Pinus mugo* were displaced by *Larix decidua* and *Picea abies*. The combination of charcoal, soil and boulder dating and soil chemical and physical characteristics has allowed the reconstruction of the events (natural- and human-driven) which occurred during the Lateglacial and Holocene period, leading to the present landscape of this small catchment of the Italian Alps.

Zusammenfassung

Die Alpine Umwelt ist ein faszinierendes Freilandlabor, in welchem man die Effekte der Kimaschwankungen während des Spätpleistozäns und frühen Holozäns untersuchen kann. Den Beginn des Holozäns vor etwa 11.500 Jahren kennzeichnete eine abrupt einsetzende und schnelle Erwärmung des Klimas. Diese bedeutende Klimaveränderung führte zu einem schnellen Rückzug der Gletscher, vergleichbar mit der heutigen Situation als Folge der globalen Erwärmung. Erkenntnisse über den Einfluss des damaligen Klimawandels auf die Landschaft können bei der Entwicklung von Zukunftsszenarien im Rahmen des globalen Klimawandels helfen. Gletscher und glaziale/periglaziale Prozesse, sowie Veränderungen in Geomorphologie und Vegetation formten das Gebiet und hinterliessen sichtbare (z.B. Moränen) und unsichtbare (z.B. fossile Böden, Holzkohle) Spuren als Beweise der Empfindlichkeit von Hochgebirgsregionen gegenüber Klimaschwankungen.

Der innovative Ansatz dieser Dissertation ist die Nutzung von Böden als natürliche Archive des Landschaftswandels durch Klimaveränderungen und menschlichen Einfluss. Der Einsatz

verschiedener Datierungsmethoden erlaubt die Anwendung unterschiedlicher Ansätze und eine präzisere Evaluation zur Verringerung möglicher Fehlerquellen.

Die vorliegende Dissertation im Gebiet der Geochronologie hat folgende Hauptziele:

- Untersuchung der ältest-möglichen Fraktion organischer Substanz in Alpinen Böden auf silikatischem Ausgangsgestein.
- Chemische Charakterisierung dieser Fraktion.
- Vergleich der ^{14}C-Alter dieser organischen Substanz mit Altern, welche durch Oberflächen-Datierungen gewonnen wurden.
- Anwendung absoluter und relativer Datierungstechniken bei denselben geomorphologischen Objekten.
- Datierung von Holzkohlen in Böden und Rekonstruktion der Vegetationsgeschichte.
- Rekonstruktion der hochalpinen Landschaftsentwicklung basierend auf ausgewählten datierbaren Objekten.

Das Ziel ist die Rekonstruktion einer Chronologie der Ereignisse in einem alpinen Tal in Norditalien vom Letzten Glazialen Maximum (LGM, ca. 20.000 Jahre vor Heute) bis zum Holozän. Die gemessenen Signale des Landschaftswandels wurden den Klima- und Gletscherschwankungen im Verlauf der letzten 18 - 20.000 Jahre zugeordnet, sowie den menschlichen Aktivitäten seit dem Neolithikum. Am Beginn der Arbeit stand die Entwicklung einer Methode zur Extraktion des stabilen Pools organischer Bodensubstanz, gefolgt von der Datierung mit der Radiokohlenstoff-Methode. Die gewonnenen Extrakte waren aliphatische und mit Stickstoff angereicherte Verbindungen, und die ältesten Fraktionen datierten auf die erste Rückzugsphase der Gletscher vor etwa 17.000 Jahren. Diese organischen Verbindungen repräsentieren Bestandteile der ersten organischen Substanz, welche nach dem Rückzug der Gletscher gebildet wurde und deren Alter somit den Ausgangspunkt der Bodengenese markieren. Im Verlauf der Arbeit konnten wertvolle Informationen zur Zusammensetzung des ältesten Pools organischer Substanz und zu den wichtigsten Mechanismen der Stabilisierung in alpinen Böden gewonnen werden. Die Bildung von Bodenbestandteilen wie sekundären Tonmineralen und Fe- und Al-Hydroxiden konnte direkt mit den Bodenaltern in Bezug gesetzt werden und/oder zu bestimmten Ereignissen während der Bodenentwicklung (z.B. Hangprozesse). Die ehemalige Ausbreitung der Gletscher im Untersuchungsgebiet wurde durch Messung kosmogener Nuklide (^{10}Be) untersucht, welche in den Oberflächen von Blöcken akkumulierten, seit sie durch Gletscher in ihre jetzige Position gebracht worden waren. Die Verknüpfung von ^{10}Be-Oberflächendatierung und ^{14}C-Datierung der stabilen organischen Substanz in Böden ergab vergleichbare und signifikante Ergebnisse, welche die Gletscherschwankungen und periglazialen Prozesse im Untersuchungsgebiet vor 17.000 bis 9.000

Jahren erklären können. Das Alter der Böden korrelierte direkt mit den Warmphasen der Referenzchronologie des Spätglazials, und somit konnte die Dauer der einzelnen Warm- und Kaltphasen im Untersuchungsgebiet bestimmt werden. Die Identifizierung und ^{14}C-Datierung der Holzkohlenfragmente verfeinerte die Chronologie des Untersuchungsgebietes. Das Alter der Holzkohlenfragmente wurde als Proxy für die Chronologie der Bodengenese genutzt (im Falle einer ungestörten Entwicklung) und zur Untersuchung der Feuer- und Vegetationsgeschichte. Für die letzten 10.000 Jahre konnten 13 Brandereignisse nachgewiesen werden, und ein möglicher menschlicher Einfluss auf 7-8 Brände in den letzten 6000 Jahren. Klimatische und anthropogene Faktoren führten zur Verdrängung von Koniferenarten wie *Pinus sylvestris* und *Pinus mungo* durch *Larix decidua* und *Picea abies*.

Die Kombination von Holzkohle-, Boden- und Gesteinsdatierungen sowie von bodenchemischen und –physikalischen Eigenschaften erlaubte die Rekonstruktion der Ereignisse (natürliche und anthropogen-gesteuerte) im Spätglazial und Holozän, welche zur Entstehung der heutigen Landschaft in diesem Gebiet der italienischen Alpen führten.

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List of manuscripts

The results of the experiment about the extraction and radiocarbon dating of the stable fraction of soil organic matter were published in *Manuscript I*. *Manuscript II* and *III* deal with the application of the soil-dating technique in combination with other numerical and relative dating techniques. *Manuscript III* gives a final and general comment on the applied methodology and on the landscape evolution of the studied sites. *Manuscript IV* contains results of soil charcoal analysis as a tool for investigating the fire and vegetation history and human impact in the investigated area.

Manuscript I

Favilli, **F.**, Egli, M., Cherubini, P., Sartori, G., Haeberli, W., Delbos, E., (2008). Comparison of different methods of obtaining a resilient organic matter fraction in Alpine soils. *Geoderma* 145, 355-369

Manuscript II

Favilli, F., Egli, M., Brandova, D., Ivy-Ochs, S., Kubik, P., Cherubini, P., Maisch, M., Haeberli, W., (2009). Combination of numerical dating techniques using ^{10}Be in rock boulders and ^{14}C of resilient soil organic matter for reconstructing the chronology of glacial and periglacial processes in a high Alpine catchment during the late Pleistocene and early Holocene. *Radiocarbon* 51, 2, 537-552.

Manuscript III

Favilli, F., Egli, M., Brandova, D., Ivy-Ochs, S., Kubik, P., Cherubini, P., Mirabella, A., Sartori, G., Giaccai, D., Haeberli, W., (2009). Combined use of relative and absolute dating techniques for detecting signals of Alpine landscape evolution during the late Pleistocene and early Holocene. *Geomorphology* 112, 48-66.

Manuscript IV

Favilli, F., Cherubini, P., Collenberg, M., Egli, M., Sartori, G., Schoch, W., Haeberli, W., (2010) Charcoal fragments of Alpine soils as the indicator of the landscape evolution during the Holocene in Val di Sole (Trentino, Italy). *The Holocene* 20, 67-79

List of abbreviations:

AAS = Atomic Absorption Spectrometry

AMS = Accelerator Mass Spectrometry

BC/AD = Before Christ / After Death

Cal BP = Calibrated ages before present

EDS = Energy Dispersive Spectroscopy

ELA = Equilibrium Line Altitude

ETH = Eidgenössische Technische Hochschule (Swiss Federal Institute of Technology)

H_2O_2 = Hydrogen Peroxide

HCl = Hydrochloric Acid

HNO_3 = Nitric Acid

HF = Hydrofluoric Acid

LGM = Last Glacial Maximum

LIA = Little Ice Age

MIR-DRIFT = Mid Infrared-Fourier Transformed Infrared Spectroscopy

NaOCl = Sodium Hypochlorite

OM = Organic Matter

SED = Surface Exposure Dating

SEM = Scanning Electron Microscope

SOM = Soil Organic Matter

Part A
Synopsis

1. Introduction

Remembering the past is a way to understand the future. For this reason, in the modern world, the most important thing is to understand the past with every minute detail. (Akkemik, 2006)

The Alpine territories have silent witnessed the great and often fast climatic changes which have occurred in the Lateglacial and Holocene period. These "rapid" climatic changes have left visible and invisible traces in the mountain regions. The retreat of the glaciers in the period following the Last Glacial Maximum (LGM 24,000 – 20,000 years ago; Kelly et al., 2004) has left behind the sediments on which the soil formation took place and the subsequent vegetation could grow (Birkeland et al., 2003). As a consequence of the drastic temperature increase after the LGM and especially at the onset of the Holocene, the glaciers have disappeared very rapidly in some regions, leaving sediments and periglacial features as evidence of their extension. The situation has some parallels today. It is significant that in the last 150 years, Alpine glaciers transitioned from a period of distinct readvancement in previously deglaciated areas, named Little Ice Age (LIA – several oscillations between the 14th century and 1850 AD; Ivy-Ochs et al., 2008), to the minimal ice extent of the past 5000 years (Haeberli, 1994; Haeberli and Hoelze, 1995; Paul et al., 2004). The Alpine landscape, slowly shaped in the last 20,000 years by glacier fluctuations and related geomorphological/periglacial processes, is one of the sites where several pre-historical human activities took place with the development of the first agricultural practises and commercial trades. The Alpine region can be considered as an open-air archive of past climate change and the effects of human activities on landscape dynamics. Both these effects can be studied by the geomorphological features deposited after the LGM (like moraines and erratic boulders) or on organic residues buried in the soils (like plant residues and charcoal fragments) with the aid of archaeological findings in nearby areas.

The aim of this work is to reconstruct the landscape evolution of the Alpine valley "Val di Sole" in Trentino, northern Italy. We investigated the oldest possible OM fraction in order to compare the ^{14}C age of this fraction and of charcoal fragments with the Surface Exposure Dating (SED) ages. We focused on the use of soils as archives of past climatic, periglacial and human events.

Large boulders lying on the morainic sediments have been dated as evidence of former glacial extents. Soils developed on moraines of different age, on slope deposits and on rockglaciers have been sampled and the oldest carbon pool has been extracted and radiocarbon dated in order to get reliable ages of the sediment deposition. Since the formation of a soil is time-dependant (Zech et al., 2003), the soil's physical and chemical characteristics can be used as a relative age indicator, giving clear evidence about the events which have characterised the site where the soil developed (i.e., increase in the skeleton fraction in the topsoil because of slope instability or rock fall). Soils often

contain specific organic compounds (charcoal fragments, buried plant residues) which can be used to study the vegetation succession, to estimate the soil age and to distinguish between natural and/or anthropogenic-induced fires. The soils provide evidence of the landscape evolution. Their development can clarify the combined effects on the natural territory evolution brought by climate, landscape and human societies. The application of relative and absolute dating techniques allows a wide investigation view and a study of the landscape through different temporal and spatial scales.

1.1 Glaciers, permafrost and their traces

Ice has a great eroding and accumulating power, and for this reason has played a dominant role in shaping landforms. The slowly moving ice abrades solid bedrock and accumulates it at the terminus and at its lateral parts (Fig. 1.1) (Strahler and Strahler, 1987).

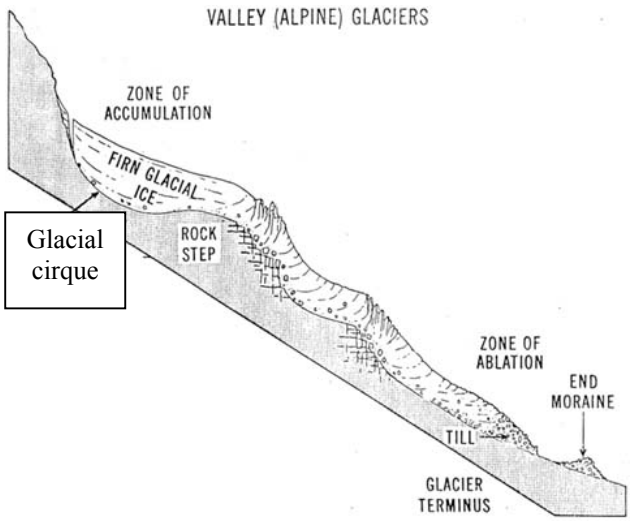

Fig. 1.1. Typical scheme of an Alpine glacier (drawn by A.N. Strahler. In: Strahler and Strahler, 1987).

The most widespread features of glacial deposition are *moraines*. Moraines are basically layers or ridges of till. *End moraines* and *ground moraines* are common to both Alpine glaciers and ice sheets. End moraines form at the terminus of the glacier. As the glacier begins to recede, a layer of till is laid down, forming a gently undulating surface of ground moraine. This ground moraine can be ten to hundreds of meters thick, substantially altering the physical environment. Successive halts in ice retreat produce successive moraines, termed *recessional moraines*. Alpine or valley glaciers also form two other types of moraine. The sides of a valley glacier accumulate large quantities of debris from the valley walls. When the glacier melts, this material is left behind as ridges called *lateral moraines*. When two advancing valley glaciers come together to form a single flow, the till that was once carried along their edges is now joined to form a *medial moraine*. Moraines can be dated directly or can be assigned to a climatic stadial (a phase) according to a variety of methods which include their relative position in the field within the regional morainic sequence, their morphological characteristics (freshness, shape, boulders size), their ELA-depression (Equilibrium

Line Altitude – difference in altitude of the morainic depositions) relative to the Little Ice Age moraines, glaciological characteristics of the paleoglaciers and the ELA of similar glaciers in the vicinity. The erratic boulders are geomorphological objects which are widely used to reconstruct past glacier extension and climate oscillations (Ivy-Ochs et al., 1996, 2004, 2006ab, 2007, 2008; Kelly et al., 2004; Kerschner and Ivy-Ochs, 2008). These rocks have been transported by the glacier on a lateral or terminal moraine or by rockglaciers (cf. below) and deposited with the debris. After the melting of the ice, these boulders built up with time a certain amount of cosmogenic nuclides (^{10}Be, ^{36}Cl, ^{26}Al) due to reactions induced by cosmic rays. The present position of these boulders is considered a limit of past glacier extension and periglacial activity. The timing of exposition is then measured using Accelerator Mass Spectrometry (AMS) (see also paragraph 1.5.2).

Rockglaciers are typical geomorphological features of a periglacial environment and characteristic of high mountain permafrost. They are defined as "steadily creeping perennially frozen and ice-rich debris on non-glacierised mountain slopes" (Haeberli et al., 2006). Rockglaciers are made up of an ice/rock mixture (the latter ranging from silty sand up to large boulders) that creeps on hill slopes at velocities depending on the geometry of the rockglacier main body, the surface of the slope and the meteorological characteristics of the site. Typical flow rates vary between a few decimetres and a few centimetres per year (Fig. 1.2) (Kääb et al., 2002; Serrano et al., 2006). The formation and the activity of a rockglacier needs the presence of perennially frozen material (permafrost) above which a seasonally frozen subsurface is formed (active layer), which mostly depends on local meteorological characteristics (Humlum, 1997; Haeberli et al., 2000; Isaksen et al., 2000; Frauenfelder et al., 2001). The initiation, growth and maintenance of active rockglaciers is related to the energy fluxes at the surface and to the thermal characteristics of the active layer. The knowledge of the interactions between atmospheric characteristics and ground thermal processes is essential to understand the age, the climatic sensitivity and the palaeoclimatic significance of rockglaciers (Humlum, 1996). Due to the considerable ice content of rockglaciers, their dynamics respond sensitively to temperature variations (extent, distribution and thickness of permafrost and of the active layer), and to temporal dimensions (formation, preservation and melting of ground ice under conditions of Holocene climate and recent atmospheric warming), making rockglaciers essential objects in palaeoclimatic reconstructions (Frauenfelder et al., 2001; Haeberli et al., 2006). The rockglaciers' development in many Alpine areas has enabled the determination of the presence of permafrost during the Egesen period down to 2000 – 1900 m asl (Frauenfelder et al., 2001).

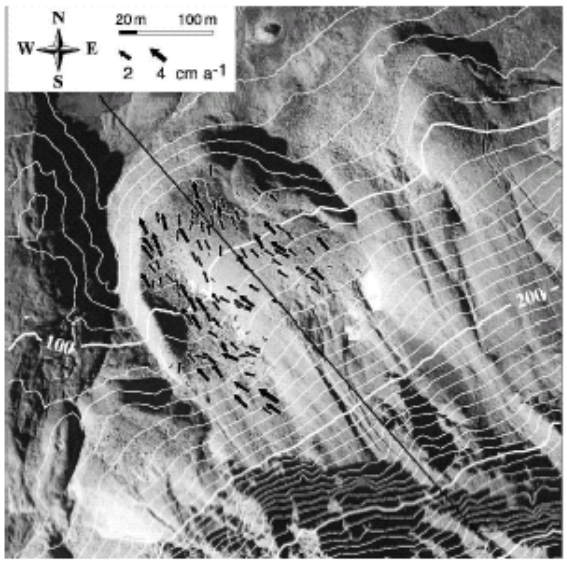

Fig. 1.2. Orthophoto 1995 of Brøggerbreen rockglacier with overlaid surface velocities as measured photogrammetrically from 1971 and 1995 imagery (from Kääb et al., 2002)

The accumulated debris, the transported boulders and the organic residues trapped in the ice reflect centuries and millennia of past frost weathering and can thus be used for reconstructing palaeoclimate and landscape evolution (Barsch, 1977; Olyphant, 1987; Francou, 1993; Barsch, 1996; Brazier et al., 1998; Frauenfelder and Kääb, 2000; Frauenfelder et al., 2001; Haeberli et al., 2003, 2006; Frauenfelder et al., 2003, 2005). Relative and numerical dating techniques like photogrammetry (i.e., Kääb et al., 2002), radiocarbon age (Hormes et al., 2008), weathering rinds (Laustela et al., 2003), Schmidt-hammer rebound (Matthews and Owen, 2008), lichenometry (Hansen, 2008), optically stimulated luminescence (OSL) (Hülle et al., 2009) and cosmogenic dating (SED) (Ballantyne et al., 2008), are typical tools to study the rockglaciers' dynamics and the climatic signal they represent (Haeberli et al., 2003). The photogrammetrically (cf. Kääb and Vollmer, 2001) estimated ages of the Murtèl (Upper Engadine) rockglacier were confirmed by ^{14}C results (all datable samples gave Holocene ages between ~8 ka and ~4ka – exposure and luminescence ages), proving that the rockglacier surfaces were indeed millennia old and that the flow of the creeping permafrost has been relatively constant over this time period (Haeberli et al., 2003; Laustela et al., 2003).

1.2 From the Würmian to the Holocene

The current Alpine environment was literally shaped by the glaciers oscillations and related periglacial processes during the Lateglacial and Holocene period (Fig. 1.3). Detailed studies on the terrestrial record of the Quaternary glaciations in the Swiss Alps have led to the conclusion that the glaciers have expanded in the foreland during at least 15 independent glaciations and that the older glaciations consisted of several glacial–interglacial phases (e.g., Habbe, 1989; Schlüchter, 1992; Jerz, 1993; Schlüchter, 2004).

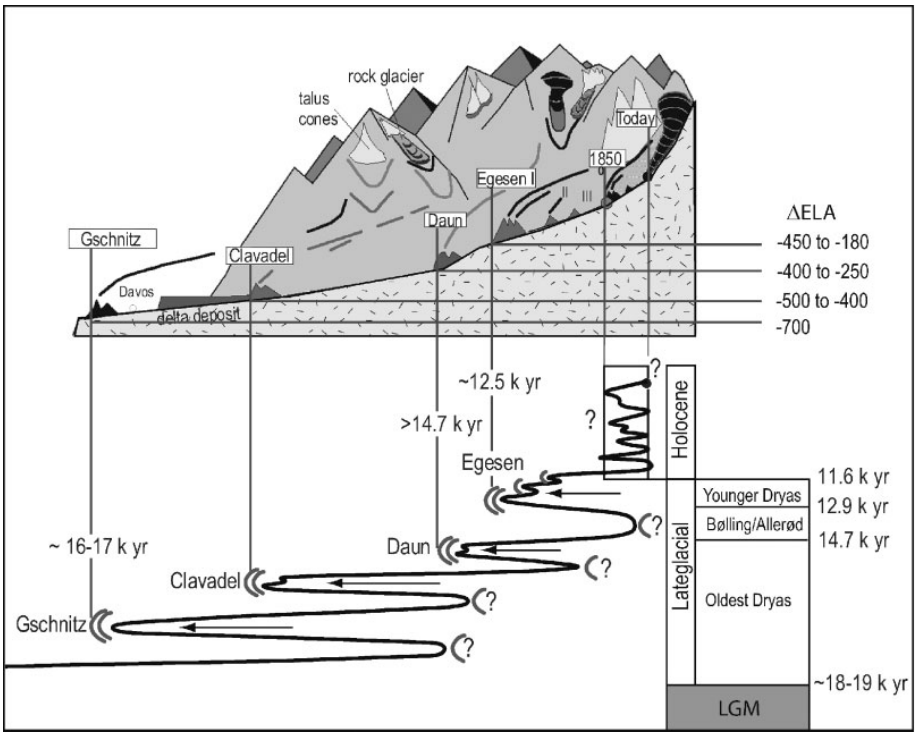

Fig. 1.3. Schematic summary of Lateglacial stadials found in the Grisons area, eastern Alps (from Ivy-Ochs et al., 2008).
ΔELA = difference of the Equilibrium Line Altitude compared to 1850 AD
kyr BP = thousand years before present
LGM = Last Glacial Maximum

The last glacial cycle (often called the "Würmian") covers the time from the end of the Last Interglacial (Eemian = Marine Isotope Stage (MIS) 5e – c. 115 ka BP) to the beginning of the Holocene (11.6 ka BP). The Würmian glaciation has been divided into Early, Middle and Late Würmian but the extension of the glaciers during the first two stages is poorly constrained and remains controversial (Fig. 1.4.; Ivy-Ochs et al., 2008).

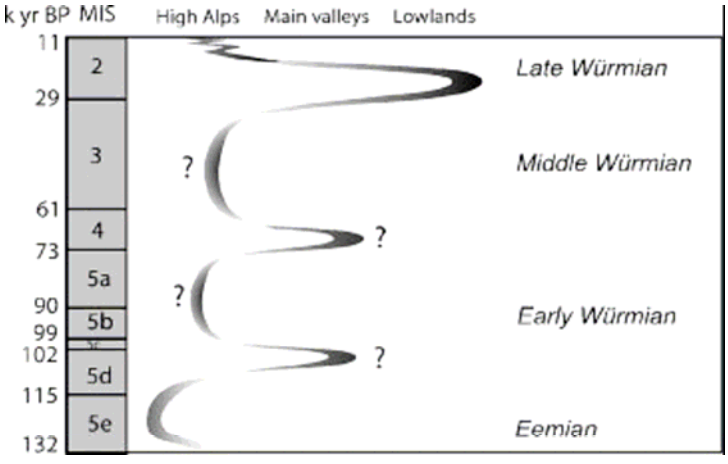

Fig. 1.4. Time-distance diagram for the last glacial cycle in the Swiss Alps and foreland (modified from Preusser and Schlüchter, 2004).
kyr BP = thousand years before present
MIS = Marine Isotope Stage

Around 30,000 years ago, large valley glaciers flowed out of the main accumulation areas and reached the mountain front. Upon reaching the lowlands, the glaciers spread out into piedmont lobes (Penck and Brückner 1901/1909). The ELA depression relative to the average Little Ice Age ELA of the individual glaciers' catchment, was in the order of 1200-1500 m (Maisch, 1981; Maisch, 1987; Schoeneich, 1999; Kerschner et al., 1999; Keller and Krayss, 2005; Ivy-Ochs et al.,

2004, 2006a,b, 2007). Terminal moraines and associated deposits formed during the LGM provide the most important morphological reference point in the forelands of the Alps. Numerous data and paleoglaciological maps are available to sketch the glaciers extension during the Late Würmian. In the area of Zürich, the Linth/Rhein glacier reached its maximum extent near the village of Killwangen (10 km NW of Zürich) between 32,900 and 24,010 cal BP (Schlüchter and Röthlisberger, 1995) and receded to the Schlieren stadial position, after which it downwasted with a marked stillstand at the Zürich stadial position at around 19,500 cal BP (Keller and Krayss, 2005). Complete deglaciation is marked by the end of meltwater influence on $\delta^{18}O$ as determined by Lake Zürich sediment which occurred before 18,030 cal BP (Lister, 1988). During the LGM the glaciers reached well into the forelands, reflecting temperature depressions around 15°C and dry conditions with 70–80% less annual precipitation than today (Haeberli and Penz, 1985). Ice at its maximum extent covered a great part of northern Europe (Fig. 1.5), Iceland, the major part of the British Islands and the whole Alpine arc until the Padana plain (Muttoni et al., 2003).

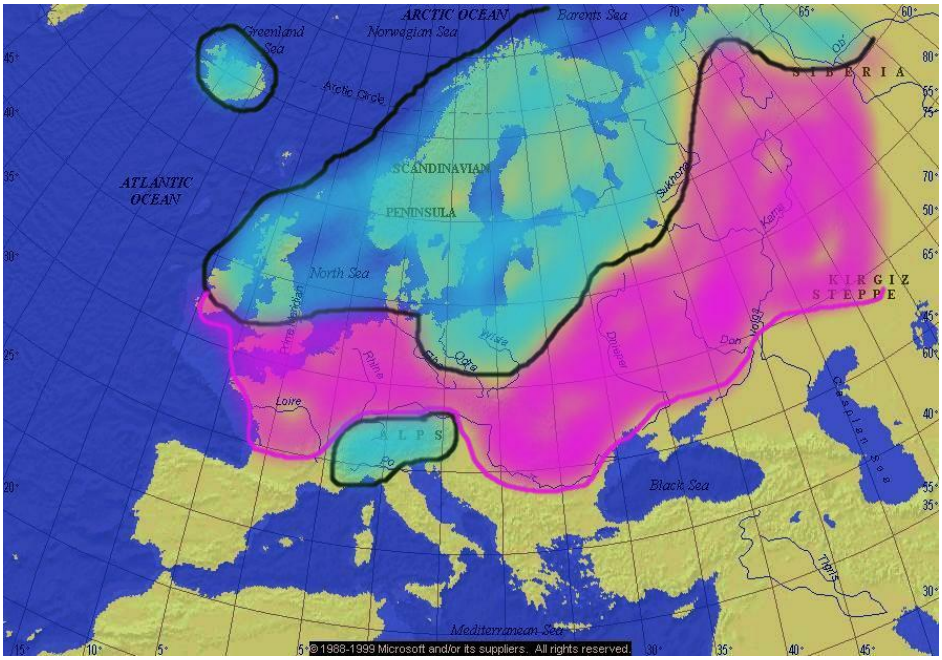

Fig. 1.5. Areas in Europe covered by the ice sheet during the Last Glacial Maximum (LGM).
= Ice
= Tundra
(www.geography.uc.edu)

Studies in the Swiss Alps (Ivy-Ochs et al., 2006a) have dated the start of deglaciation after the LGM between 21,000 and 17,000 years ago. After the peak of the LGM, the disintegration of the foreland piedmont lobes made the onset of the "Alpine Lateglacial" (Penck and Brückner, 1901/1909). During the Lateglacial, a period of just under 10,000 years, glaciers intermittedly readvanced several times to successively smaller positions leaving prominent moraines in the valleys and cirques. Traditionally, these stadials are considered as glacier tongues in equilibrium with the climatic environment after an advance over an ice-free terrain (Ivy-Ochs et al., 2008).

The initial downwasting of the Late Würmian glaciers may have taken no more than a few centuries (van Husen, 2000). Investigations of ice cores (e.g. Johnsen et al. 1992; 2001) and global sea level records (e.g. Yokoyama et al. 2000; Lambeck et al. 2002) have documented that the deglaciation occurred worldwide in the period 18–15 ka BP (Oldest Dryas). During these three millennia, the Alps were affected by at least three readvance phases namely Gschnitz, Clavadel and Daun (Maisch, 1981, Maisch et al., 1999; Ivy-Ochs et al., 2006b). During the Gschnitz stadial the glaciers consisted of 10-20% of the Late Würmian ice volume and advanced over an ice-free terrain for considerable distances, leaving prominent moraines which incorporated a large number of sediments (Kerschner et al., 2002; Ivy-Ochs et al., 2006b, 2008). This stadial is thought to have occurred around 18–17 ka BP (van Husen, 2004; Vescovi et al., 2007) after a distinct warming phase. After the Gschnitz stadial, glaciers in the Alps readvanced again with glacier tongues at higher altitudes, leaving prominent morainic deposits (Clavadel and Daun stadial, 16.5 – 15.5 ka BP). The period between about 15.5 and 12.9 ka BP has been recognized as a period of rapid warming, named the Bølling-Allerød interstadial, which led to a strong retreat of the Alpine glaciers (Alley et al. 1993; Ohlendorf, 1998; Maisch et al. 1999; Schaub et al. 2008). The overall trend of deglaciation was interrupted by a new cold phase which occurred between 12.9 and 11.6 ka BP (Younger Dryas [Egesen]- Maisch et al. 1999). This period is well represented in the Alps by typical geomorphological characteristics of the morainic sediments (sharp, blocky crests and multi-walled moraines, often named Egesen I, II and III) (Maisch, 1981, 1987; Sailer et al., 1999; Kerschner et al., 2000; Kelly et al., 2004; Ivy-Ochs 2004, 2006a, 2009). ELA depressions associated with the Egesen maximum moraines are in the order of 200 m, with extremes up to 400 m (Maisch, 1981; 1987). The glaciers' readvance during the Egesen was a reaction to climatic fluctuations, which were mainly caused by a change in the North Atlantic Ocean circulation and subsequent weakening of oceanic heat transport to high latitudes (Kerschner and Ivy-Ochs, 2008). Surface exposure dating of Egesen moraines from many Alpine catchments in the Swiss Alps suggests an average timing of moraine stabilisation around 12,300 cal BP and a final stabilisation around 11,300 cal BP (Ivy-Ochs et al., 2006a). At the end of the Younger Dryas and beginning of the Holocene, the climate changed very rapidly (a few decades – Alley, 2000) with increasing dry conditions which led to the final glaciers downwasting.

^{10}Be data presented in Ivy-Ochs et al. (2009) provide an age for the post-Younger Dryas cold oscillations of 10.8 – 10.5 ka which support the Preboreal readvance (Palü glacier readvance; Ivy-Ochs et al., 2006a). The period between 10.5 and 3.3 ka saw the establishment of climatic conditions not conducive enough to significant glaciers' readvance, except during rare brief intervals. During most of this period, the treeline was higher than today and three distinct warm

intervals were identified around 9.2 ka, from 7.5 to 6.6 ka and from 6.2 to 5.6 ka (Ivy-Ochs et al., 2009). This warmer trend was interrupted by short phases of glacier-friendly climate before 9.2 ka, around 8.85 and 8.4 ka, between 6.3 and 5.0 ka and after 3.8 ka (Ivy-Ochs et al., 2009 and references therein).

1.3 Weathering and soil formation

Weathering is defined as the chemical and physical alteration of rocks at or near the Earth's surface caused by effects from atmospheric elements (Birkeland, 1999). The process of weathering begins as soon as a surface (i.e., a morainic sediment) is exposed. Colonisation by vegetation contributes to the chemical and physical weathering of the surfaces and to the stabilisation of the slopes (Matthews, 1992). Physical weathering processes expose fresh rock and surface to chemical weathering, whereas chemical weathering reduces the strength of rock, making it susceptible to physical breakdown (Anderson et al., 2002). The process of physical weathering does not change the chemical and mineralogical composition of the original rock. Chemical weathering reduces the strength of rock and includes the partial dissolution of bedrock by superficial fluids (i.e., organic acids produced by the plants) and removal of soluble ions in dissolution (Anderson et al., 2002; von Blackenburg, 2005). Chemical weathering of rocks is very important for the generation of soils, for the evolution of the landscape, and as a main source of inorganic nutrients for plant growth and therefore for life. In nature physical and chemical weathering occur together and are inextricably connected. Materials released during weathering are removed from the system either by leaching water or react in the system to form a variety of crystalline and amorphous products like clay minerals and hydrous oxides of iron and aluminium (Nettleton and Brasher, 1983). In most cases, clays are a weathering product of the uppermost layer. The formation and stability of the clays depends on the precursor minerals and the conditions of soil development, as they are sensitive to temperature and pressure variations. Since the soil properties associated with the weathering of the primary minerals develop rather slowly, they can be used as a relative indicator of the surface age (Birkeland, 1999). Studies on Italian and Swiss Alpine soils (e.g., Egli et al., 2001b, 2003b, 2006) have demonstrated that the amount of weathering end-products like smectite and vermiculite can be directly related to the age of the surface.

The mass balance approach provides crucial information about the weathering effect on a certain site. The losses or gains of the elements during pedogenesis, compared to the mineralogical composition of the parent material, delineate the weathering stage and indicate the relative age of the soils (cf. Egli and Fitze, 2000, Egli et al., 2001a, 2003a, 2004, 2005, 2006).

A soil can be defined as a transition phase as the rock changes to more stable chemical states. A soil is a function of a number of independent state factors such as parent material, climate, topography, age and role of organisms (Jenny, 1941, 1980; Dokuchaev, 1967; Bohn et al., 1985; Phillips et al., 2008). Soil formation in the broad sense is the result of synergetic processes of self organisation of an *in situ* soil system as it functions in time and space. Soil formation, *sensu stricto*, is the transformation of the solid phase lithomatrix (parent material) of the soil system into the pedomatrix (soil body, soil mantle) (Targulian et al., 2007). Soils are open systems and present a high variability in their morphology and taxonomy because they depend on the impact of the different environments and of the soil-forming factors (Birkeland et al., 2003; Dixon and Thorn, 2005). Targulian (2005) expressed this dependence in a more complete way as: factors of soil formation → internal soil system functioning → specific pedogenic processes → soil properties and features → external soil functions. For this reason, the soils developed in the Alpine environment are mainly related to the warm phases of the Lateglacial and of the Holocene. Determining the age of the Alpine soils is essential for understanding the landscape evolution and climate oscillations during the Late Pleistocene and Holocene period (Mayer et al., 2008). Soils can be used as archives of changing weathering conditions and landscape evolution. Their chemical and physical development gives an indication of the relative age of glacial deposits (Jacobsen, 1990; Munroe, 2008). Alpine soils developed on silicatic parent material always demonstrate a low pH and an abundant sand fraction (Baroni and Carton, 1991; Mirabella and Sartori, 1998; Sartori et al., 1997, 2005; IUSS Working Group WRB, 2006). Soils with profile A-C, A-R (*[Hyper-skeleti]-Umbrihumic Leptosols*) or OA-C, OA-R (*Dystri-Folic Histosol*) and with a depth up to 40 cm are the typical soils of the Alpine meadows dominated by *Carex curvula*, between 2200 and 2700 m asl. The range 1800-2200 is characterized by ranker or podzols with a typical horizon sequence A(OA)-Bh(Bhs)-(Bs)-C (*[Episkeleti-] Humic Umbrisol, Enti-Umbric [Histic] Podzols, [(Episkeletic)], [(Episkeleti-)] Entic Podzols* and *Umbri[Histi]-Densic Podzols (Skeletic)*). The north-facing slopes and the upper montane zone, down to the subalpine zone (1300-2000 m asl), are characterized by very acidic podzols with the horizons A(OA)-E-Bhs-Bs-(BC)-C *(Skeleti-Entic Podzols)*. These soils are typical of a very acidic environment with intense leaching and podzolisation process. South-facing surfaces and those between 800 and 1300 m asl show a lower or absent podzolisation and are dominated by Cambisols with an horizon sequence AE-BA-Bs-(BC)-C[CR] *(Dystri-Skeletic Cambisol, Dystric Cambisols, Chromi-Skeletic Cambisols (Dystric), Dystri-Chromic Cambisols)*. The time needed for a complete Podzol development can vary between 350–1000 years in a very wet, relatively mild climate (Singleton and Lavkulish, 1987), and 3000–10,000 in Michigan (USA) with a mean annual temperature of 5.2 – 6.2°C (Barett and Schaetzl, 1992).

Other typical Alpine soils are Cryosols, Fluvisols, Regosols, Leptosols, Histosols and Gleysols (IUSS Working Group WRB, 2006). Cryosols occur on top of the Alpine belt (> 2600 m. a.s.l.) and are very sensitive to changes in temperature. They are associated with the specific belt where soil temperature is at or below 0°C for at least 2 years in succession. They show evidence of cryogenic processes, cryoturbation and contain water in solid form (permafrost condition).

Fluvisols usually relate to genetically young, azonal soils on the more stable portion of alluvial cone, on the high Holocene terraces (Previtali, 2002) and lacustrine deposits.

Regosols are young soils, composed of a wide variety of textures and it is possible to find them in a variety of different conditions. In the Alps they occur on the belt of meadows in a very limited environment (Jabiol et al., 1995; Chersich et al., 2006).

Leptosols, being undeveloped soils, are shallow or extremely gravely over continuous rock (within 25 cm of the soil surface) (Jabiol et al., 1995; Chersich et al., 2006).

1.4 Soil organic matter and stabilisation mechanisms

Soil Organic Matter (SOM) is made of a wide spectrum of materials, ranging from a complex mixture of microbiologically-derived compounds (Stevenson, 1994) to undecomposed plant and animal tissues and humus, the latter being defined as "colloidal soil organic matter that decompose[s] slowly and colours soil brown and black" (Singer and Munn, 1987). Humus commonly makes up the bulk of Soil Organic Matter. SOM is found in varying amounts in Alpine soils and is always most concentrated in the uppermost horizons (O, A/AE). SOM is important for many soil properties, particularly for the formation of surface soil structure and for reactions which occur during pedogenesis (Ugolini and Sletten, 1991). Worldwide, the organic matter stored in soils (2157 – 2293 Pg) is almost three times that in the atmosphere (760 Pg) and is about two to three times that which is accumulated in living organisms in all Earth's terrestrial ecosystems (Gonzàlez-Pérez et al., 2004). SOM represents one of the largest reservoirs of organic carbon on a global scale (Schlesinger, 1995). The global carbon cycle is strongly dependent on the turnover of SOM (Schlesinger,1991; Lal, 2001). Because of the importance that SOM has for the global balance of CO_2 (Schlesinger, 1995, Lal, 2004), the study of its stability and potential biodegradability in a warmer environment is currently one of the topics of highest interest in the scientific research (Sjögersten et al., 2003; Uhlířová et al., 2007).

Part of the organic carbon (the "fresh" addition) is easily mineralised, whereas another carbon pool degrades slowly at timescales from hundreds to thousands of years (Oades, 1995). Three key processes have been proposed to explain the formation of this passive or long-residence-time SOM fraction: (i) selective preservation due to chemical recalcitrance, i.e. stabilisation due to the

structural properties of the organic matter, such as plant litter, rhizodeposits, aliphatic compounds and charred OM; (ii) inclusion of organic matter into aggregates or micropores, leading to physical protection of organic matter from microbial attack; (iii) stabilisation by interaction with mineral surfaces (Fe-, Al-, Mn-oxides, phyllosilicates) and metal ions (Anderson and Paul, 1984; Sollins et al., 1996; Baldock and Skjemstad, 2000; Eusterhues et al., 2003; von Lützow et al., 2006). The contribution and relative importance of these stabilisation mechanisms in different soils is not fully understood. The amount of C storage in a soil is controlled mainly by two factors: i) input by net primary production (its quantity and quality) and ii) by its decomposition rate. Decomposition of natural OM in soil is primarily microbially mediated, with about 10-15% of the energy of organic C utilised by soil animals (Wolters, 2000). The OM decomposition usually passes through three phases, which also characterise the type and the turnover time of the organic material. The first phase defines the *labile* OM as the more recently added and more active OM pool. The turnover time is around a few years in a temperate climate (Jenkinson and Ladd, 1981). The second phase shows a slower decomposition rate, in the order of 10-100 years. This fraction is defined as the *intermediate* OM. The third phase defines the *recalcitrant and mineral-protected* OM and shows very slow decomposition rates of about 100-10,000 years or more. This C pool is responsible for the long-term stabilisation of OM in soils (Fallon and Smith, 2000).

The use of chemical reagents to remove (mineralise) the younger pools of the organic matter have shown that oxidation-resistant OM is relatively enriched in aliphatic, aromatic and amide compounds (i.e., Theng et al., 1986; Leifeld and Kögel-Knabner, 2001; Helfrich et al., 2007; Favilli et al., 2008; Egli et al., 2009). Aliphatic materials are a heterogeneous group of compounds, characterised by a high hydrophobicity, which can prevent access for degradating enzymes. It has also been shown that polyethylene chains can adsorb on clay surfaces or intercalate between phyllosilicates in a flat extended conformation in an acid environment (Theng, 1979). The polymers which are most resistant to degradation contain aromatic rings (lignin and charcoal) and a range of polymethylenic molecules, such as lipids, waxes, cutin and suberin (Derenne and Largeau, 2001).

Density fractionation is a widely-used method to verify the protection mechanism of OM by the organo-mineral association. Density fractions are used to distinguish organic matter which is not firmly associated with soil minerals (= light, labile, active fraction) from organic matter having stronger organo-mineral associations (= heavy, resistant fraction) (e.g., Christensen, 1992; Egli et al., 2009). The light fraction is assumed to consist of less-decomposed plant and animal residues, whereas the heavy fraction is believed to encompass organo-mineral associations (Swanston et al., 2005).

The charred material is also often reported as one of the most stabilised forms of OM. Fire can create a range of complex, highly condensed aromatic compounds, chemically known as black carbon (BC) or charred organic matter, which represents a continuum from partly charred material to graphite and soot particles. The estimated residence time (confirmed by radiocarbon dating results) is in the order of 500 – > 10,000 years (Schmidt et al., 2002; Kaal et al., 2008). Charred OM is stabilised in the soils by selective preservation and by the interaction with the mineral matrix (Brodowsky et al., 2005).

It is obvious that in a soil and even in a soil horizon several stabilisation mechanisms operate simultaneously but at different degrees. For this reason, it is almost impossible to formulate a "general law" about SOM degradation, stabilisation and depth penetration. Soils have to be studied with the local environment, microclimate and vegetation where they develop. In Alpine ecosystems SOM may be protected not only by the above-cited mechanisms, but also by the low soil temperature (Hobbie et al., 2000; Mikan et al., 2002), both of which constrain OM decomposition. The processes of SOM stabilisation are temperature-dependent. Biotic and abiotic degradation and condensation, reactions that produce new aromatic structures with larger molecular weights, are slowed down by low temperatures. Moreover, the formation of organo-mineral associations is slowed down too, as the partial oxidation of organic molecules necessary to promote absorption on mineral surfaces and/or binding with metal ions is also temperature-dependent (Grünewald et al., 2006). SOM in cold environments is generally scarcely decomposed, has a low humification degree and high C/N ratio, and may become buried in the deep soil layers through cryoturbation (Bockheim and Tarnocai, 1998).

Although all soils contain carbon and consequently, therefore, in theory, can be dated by radiocarbon (^{14}C – see below), the dynamic nature of the soil system means that they receive organic matter over a protracted time period. Any radiocarbon date performed on a bulk soil will be an average age of the different OM compounds within the soil and will not give any indication about the "real" age of a soil. Measured radiocarbon ages of Soil Organic Matter are generally younger than the true age of the soil (Wang et al., 1996). Further complications arise from the circulation of humic acids, root penetration, earthworm and other biological activities. All this makes soils one of the most difficult materials to date using the radiocarbon technique (Matthews, 1985).

The theoretical isolation and radiocarbon dating of a part of the first organic matter pool, formed in Alpine soils just after the deposition of the sediments, can give an age of the deglaciation and the time needed for the establishment of the vegetation and soil formation, and could thus contribute to a deeper knowledge of the Lateglacial and Holocene landscape formation.

1.5 Application of dating techniques in the Alpine environment

From the beginning of the 20th century, the researchers have started to be interested in studying the Quaternary deposits with climatic-environmental changes (Penck and Bruckner, 1901/1909). Many authors have described glacier fluctuations in the Alps during the Holocene (e.g., Holzhauser, 1984; 2005; Hormes et al., 2001; Joerin et al., 2006, 2008). However, only a few of these studies include reliable absolute ages (Heitz et al., 1982; Maisch, 1987; Schlüchter, 1988; Kerschner et al., 1999; Ivy-Ochs et al., 2006a,b, 2007, 2008) because of the various limitations of the dating methods and the rareness of optimal representative sampling sites.

1.5.1 Relative soil dating techniques used in this thesis

Soil surfaces can be used as indicators of landscape history. There exist several techniques to relatively date a surface by analysing soils, based on the fact that soil development is time-dependent (Jenny, 1941; Zech et al., 2003). Some of the relative dating techniques analyse the degree of degradation or chemical alteration on rock surfaces or in soils, to establish a relative order of age. Studies into the effects of weathering on soil formation have been carried out in the Italian Alps (especially in the Trentino region) with respect to the development of podzol features, clay minerals and mass balance calculations (e.g., Mirabella and Sartori, 1988; Egli et al., 2001a,b, 2009) as major representatives of the Alpine soil development.

Podzolisation process:

The different solid phases of Fe and Al provide valuable information for dating. With increasing time of soil development, more Al and Fe migrate from the eluvial (E) and accumulate in the spodic horizon (illuvial – Bs/Bhs) (Fitze, 1982) from which information can be inferred about the stability of the surfaces and slope processes which occurred.

Clay minerals:

Soil mineralogy reflects the development of the individual sites. During soil formation, the phyllosilicates of the clay fraction go through several transformation and crystallisation stages which modify their mineralogical characteristics. The presence of minerals like smectite or vermiculite in Alpine soils is due to strong leaching and weathering conditions (Carnicelli et al., 1997; Mirabella and Sartori, 1998; Egli et al., 2003b) and is directly related to the weathering status of the soil.

Mass balance calculation:

The chemical characterisation leading to the formation of the soil surfaces (Podzols in particular) and the elemental mass balances can provide detailed insights into the processes of a soil and also indications about its age. Long-term weathering rates of soils can be derived from the calculations of enrichment/depletion factors, determined using immobile element content such as Ti, comparing the most weathered horizon with the parent material. Zr and Ti are considered to be two of the most immobile elements in soils (Langley-Turnbaugh and Bockheim, 1998; Egli and Fitze, 2000).

1.5.2 Numerical (absolute) dating techniques

Radiometric dating techniques are based on the fact that certain naturally occurring elements are unstable and undergo spontaneous changes in their structure and organisation in order to achieve more stable atomic forms. This process is known as "radioactive decay" and it is time-dependent. In all radioactive nuclides, the decay rate is exponential and is usually measured in terms of the time that is required to reduce a given quantity of a parent nuclide to one half (Table 1.1).

Radiocarbon dating:

Radiocarbon dating, despite the fact that it is applicable to only a relatively short span of Quaternary time (around 50,000 years), is perhaps the most often used method of all radiometric techniques. Carbon has three isotopes which are present in the atmosphere always at an equilibrium rate (^{12}C = 98,982%; ^{13}C = 1.108%; $^{14}C = 10^{10}$%). Both ^{12}C and ^{13}C are stable isotopes but ^{14}C is not and it decays to a nitrogen stable form, ^{14}N, through the emission of beta (β) particles. ^{14}C atoms are produced in the upper atmosphere through the interaction between cosmic ray neutrons and nitrogen. Through this process, ^{14}C becomes part of the C-cycle and is assimilated by plants through the photosynthetic process. After the death of an organism, the ^{14}C isotope is not assimilated anymore and loses half of its amount every 5568 years (half life - $t_{1/2}$). The method of radiocarbon dating is based on the calculation by AMS of the ratio of ^{14}C to ^{12}C. The calendar ages are obtained using a calibration program (OxCal 4.0.5; Bronk Ramsey, 1995; 2001) based on the IntCal04 calibration curve, which expresses the variation during the last 50,000 years in the atmospheric ^{14}C (expressed as $\Delta^{14}C$). IntCal04 comes from the improvement of the former calibration curve (IntCal98) based on dendrochronology data, uranium-series and radiocarbon dates on fossil corals, coupled with radiocarbon-dated organic materials from laminated marine sediments in the Cariaco Basin, Venezuela (Reimer et al., 2004). A comparison between the two curves shows the minor calibration uncertainties in the IntCal04 curve (Fig. 1.6).

Table 1.1. Summary of nuclide characteristics (modified from Gosse and Phillips, 2001)

Nuclide	Half-life	Other isotopes	Suitable targets	Target elements	Applicable time range
^{10}Be	1.5 Ma	^{9}Be	Quartz	O, Si	Several million years
^{14}C	5.56 ka	^{12}C, ^{13}C	Organic, Quartz	O	up to 50 ka
^{26}Al	0.7 Ma	^{27}Al	Quartz	Si	Several million years
^{36}Cl	0.3 Ma	^{35}Cl, ^{37}Cl	All rock types, incl. carbonates	K, Ca, ^{35}Cl	up to 1 Ma
^{3}He	Stable	^{4}He	Olivine, pyroxene	Many	Million of years

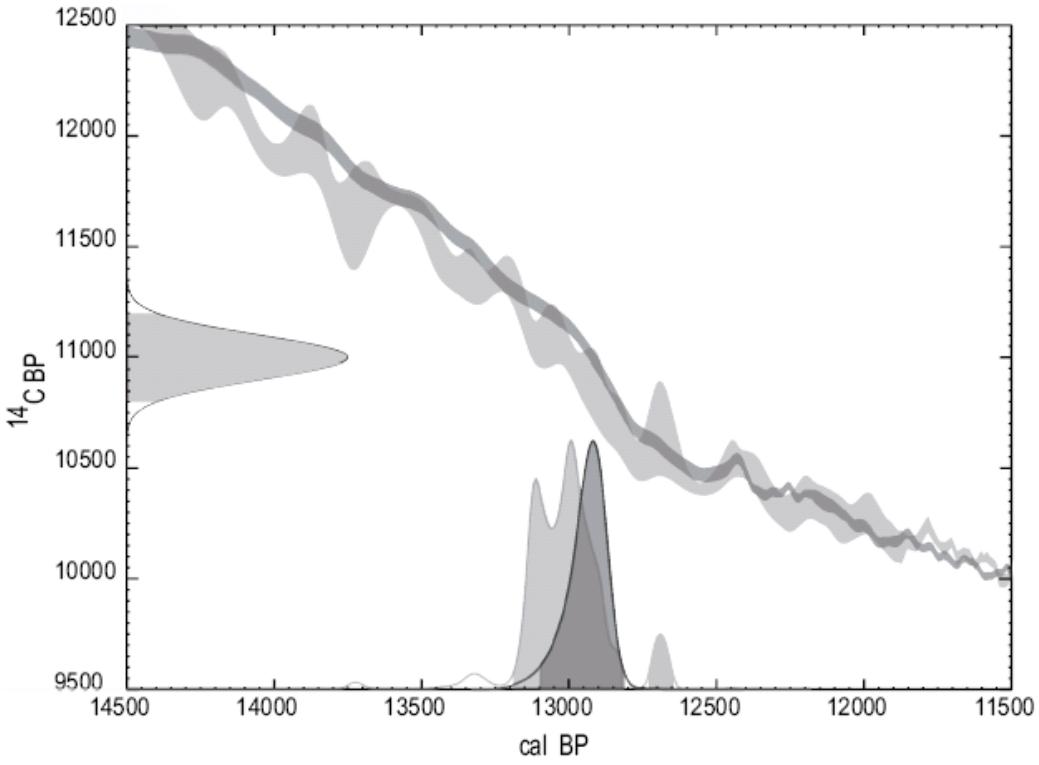

Fig. 1.6. Calibrated probability distributions for a hypothetical ^{14}C age of 11,000 ± 100 calibrated with IntCal98 (light gray) and IntCal04 (dark gray) showing 95% cal age ranges (from Reimer et al., 2004).

Calibrated ages are always expressed in terms of "cal BP" (referred to 1950 AD) or "BC/AD" and are expressed in terms of probability, usually in the 2 σ range (minimum and maximum value – 95.4% probability). For this reason, dates are reported as a range (*Tables 5a* and *5b)*, in order to reflect these uncertainties. Calibration gives an approximation of "true" age, but is still a relatively imprecise tool and must be treated accordingly. The main problem for the ^{14}C dating of bulk SOM is that the heterogeneity of the different organic components is reflected by their highly variable radiocarbon ages. Therefore, the ^{14}C dating of SOM is always difficult to interpret (Rethemeyer et al., 2004). Radiocarbon dating has been used to investigate the properties of organic matter and its mean residence time, and to estimate the age of the Alpine soils (Calderoni et al., 1998; Wang et al., 1996; Wagner, 2005; Tonneijck et al., 2006; Favilli et al., 2008, 2009a,b, 2010).

Terrestrial in situ *cosmogenic nuclide dating (TCN):*

High-energy cosmic rays entering the atmosphere consist primarily of protons and α particles. They collide with nuclei triggering a cascade of high-energy neutrons that bathe the Earth's surface. The collision between these neutrons and muons and target nuclei within certain minerals leads to the breakdown of those nuclei into fragments (a process called spallation) and the creation of new nuclides. Cosmogenic nuclides such as ^{10}Be ($t_{1/2}$ = 1,510,000 years), ^{26}Al ($t_{1/2}$ = 716,000 years), ^{14}C ($t_{1/2}$ = 5568 years) and ^{36}Cl ($t_{1/2}$ = 301,000 years) are produced through spallation and muon capture (Lal, 1991; Cerling and Craig, 1994; Gosse and Phillips, 2001). Cosmogenic nuclides build up predictably with time within the lattices of minerals but production due to spallation decreases exponentially with depth, thus the majority of nuclides occur in the few upper centimetres of the exposed rock. Cosmogenic nuclides provide a unique tool for determining ages of landforms and rates of geomorphic processes. Ratios of the radionuclide vs. the stable isotope (e.g., ^{10}Be to ^{9}Be) are measured using AMS. Quartz is well suited for ^{10}Be, ^{26}Al and ^{14}C exposure dating, since quartz is ubiquitous and its tight crystal structure makes it a closed system to either gain or loss of the isotope of interest. Atmospheric ^{14}C and ^{10}Be contamination can be removed from the surfaces and crevices of the quartz grains with acid etching (Kohl and Nishizumi, 1992). Surface Exposure Dating (SED) with ^{10}Be has been utilized to distinguish the different phases of glacial retreat and readvancement at various sites in the European Alps, New Zealand and United States (Ivy-Ochs, 1996; Balco et al., 2002; Ivy-Ochs et al., 2004, 2005, 2006a,b, 2007, 2008; Bentley et al., 2007; Hormes et al., 2008; Kerschner and Ivy-Ochs, 2008). The position of the boulders is directly related to past glacier extension and climatic oscillations. A number of articles provide detailed reviews as well as comprehensive reference lists (Gosse and Phillips, 2001; Cockburn and Summerfield, 2004; von Blackenburg, 2005; Ivy-Ochs et al., 2008).

1.6 Investigation Area

The Trentino region is one of the most complex regions of Italy from a geological perspective. Several lithotypes are present and the mineralogical and chemical composition of the rocks show a great variation within the region. The oldest rocks of the Trentino are from the first alpine formation and are represented by the metamorphic basement of the Ortles-Cevedale Massive, constituted by gneiss, micaschists, mica, feldspars and quartz. Rocks of the pre-Permian period can be found in the mountain ridges of the Adamello-Brenta and are constituted mainly of quartz, biotite and amphiboles. During the Triassic period, the Trentino region was affected by a sedimentation environment, first continental, then marine. The sediments belonging to this period are composed of carbonates and organic material. During the Miocene, the Trentino region was a depression flooded

by the sea (Prosser, 1990; Mancabelli and Sartori, 1998) and was affected by several processes of uplifting and burying, shaping the present morphological aspect of the region. During the Quaternary, the sediments left by the glaciers have covered the Palaeozoic, Mesozoic and Cenozoic rock formations. These incoherent sediments vary in their thickness from few centimetres to hundreds of meters. The sediments consist of aeolian, morainic, rock falls or alluvial deposits. The glacial deposits are characterized by a high heterogeneity in their mineralogical and granulometric composition. Usually they are characterized especially by skeleton and sand but the silt-clay component can be significant. The soil surfaces we can see nowadays come from the pedogenesis which occurred above these substrates.

The study area comprises parts of Val di Sole, Val di Rabbi and Val di Pejo in the southern Alpine belt in northern Italy. The entire area developed upon a siliceous parent material (paragneiss, micaschists), covered by Quaternary deposits. The Val di Sole is a dry, inner-alpine valley. The glaciers present today are located in the mountain region of Monte Cevedale (Ortles-Cevedale group; Baroni et al., 2003) to the North-West of the investigated valleys. The climate of the valleys ranges from temperate to alpine (above the timberline). The mean annual temperature ranges from 8.2°C (valley floor – around 800 m asl), to 6.8°C at 1580 m asl and to 0°C at 2400 m asl. Mean annual precipitation ranges approximately from 800 to 1300 mm/year (Servizio Idrografico, 1959; Provincia Autonoma di Trento, 1996) (Fig. 1.7, 1.8 and 1.9).

Heathland and shrubland occurring above 1500 m asl is composed mostly of *Alnus viridis* (Chaix) DC, *Juniperus communis* L., *Rhododendron ferrugineum* L., *Vaccinium myrtillus* L. and *Vaccinium uliginosum* L.. Low altitude forests are dominated by *Castanea sativa* Mill., *Carpinus betulus* L., *Acer pseudoplatanus* L. and *Fagus sylvatica* L.. The timberline is close to 2100-2200 m asl and the forests are dominated, at higher elevation, by the conifers *Larix decidua* Mill. and *Picea abies* L. (Pedrotti et al., 1974). Areas above 2300 m asl are covered with rocks, boulders and short-grass meadow dominated by *Carex curvula* Al. and *Nardus stricta* L.

The investigation sites were between 1500 and 2500 m asl.

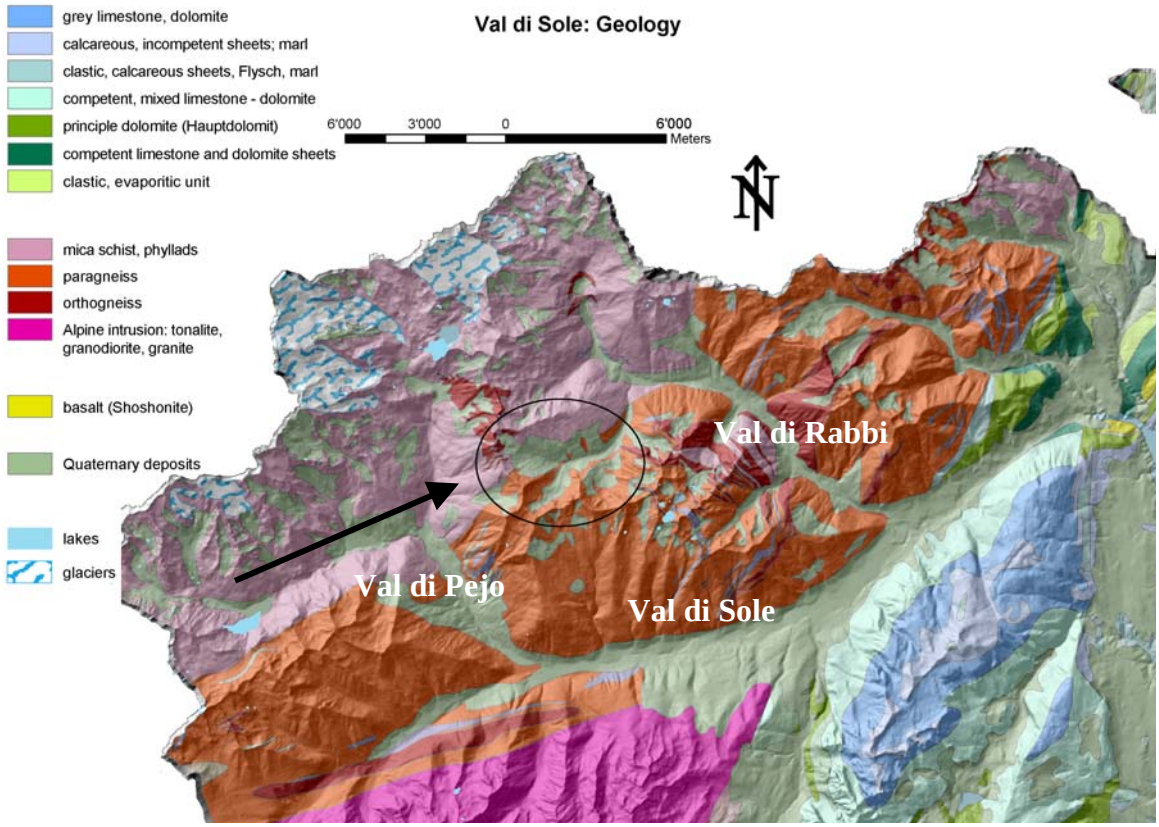

Fig. 1.7. Geology of the north-west part of the Trentino region with indication of the investigation area (modified from Provincia Autonoma di Trento, 1996)

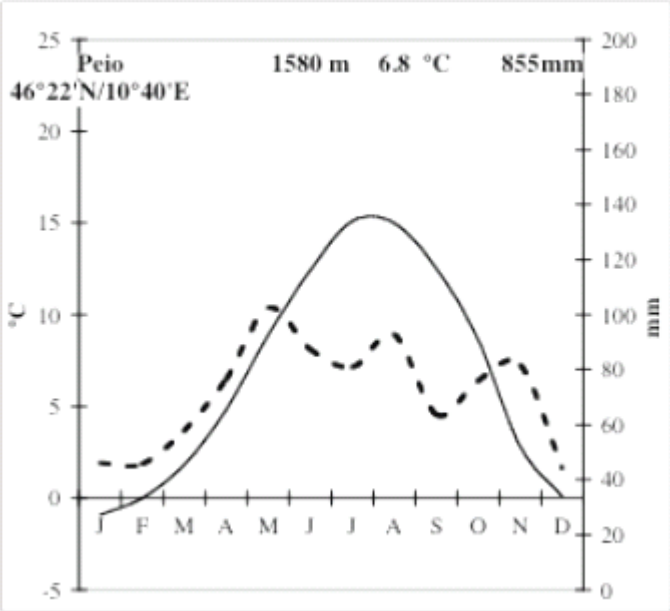

Fig. 1.8. Mean Annual Temperature and Mean Annual Precipitation at the Pejo meteorological station (Provincia Autonoma diTrento, 1996)

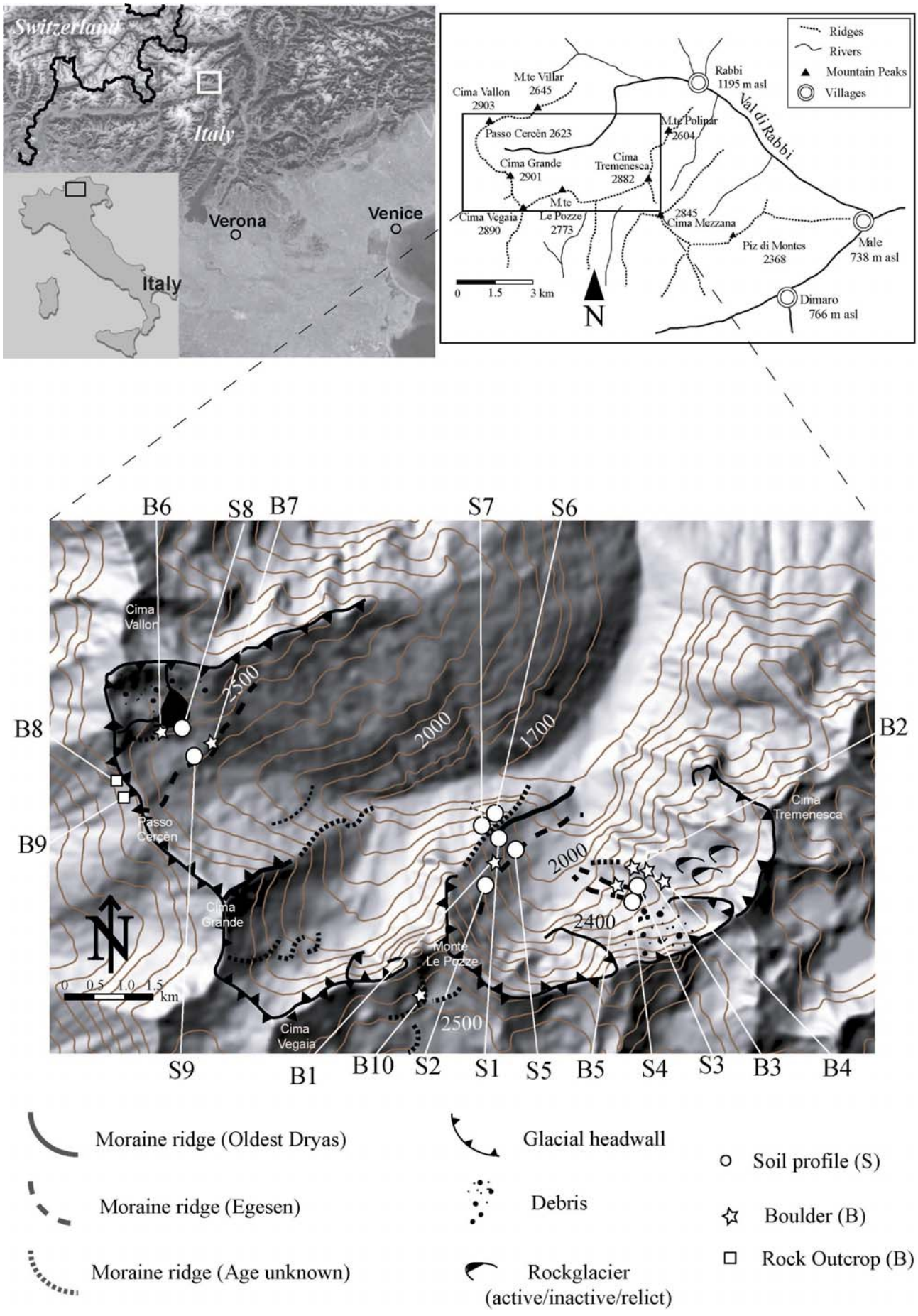

Fig. 1.9. The study area with the location of the investigated sites

Interesting geomorphological situations can be found at varying altitudes in these valleys with pronounced periglacial features such as rockglaciers and Lateglacial moraines, which provide opportunities to date the retreat stages of the glacier. The Val di Sole had not yet been studied from a geochronological point of view, so the morainic sediments were of unknown age. Moraines were tentatively attributed to the Lateglacial stadials according to their position within the valley and relative to other moraines (shape, freshness of the landforms and boulder content).
Many rockglaciers in the area are still active but some of them present an initial development of vegetation and soils (Fig. 1.10).

Fig. 1.10. Rockglaciers in the glacial cirque delimited by Cima Tremenesca and Monte le Pozze at 2450 m asl

According to the moraines description found in Ivy-Ochs et al. (2008) and to their relative position, most of studied moraines probably belong to the Younger Dryas (Egesen) glacier readvance(s). No Little Ice Age moraines were found at higher altitudes and, according to the timing of the soils development and boulders deposition (see below), it is likely that these valleys and cirques were completely ice-free already at the onset of the Holocene climatic optimum (around 9000 years ago) (Joerin et al., 2008). Therefore, the calculation of the ELA depression was not possible. No radiocarbon and beryllium dating was ever performed in the valley or in its vicinity and the timing of deglaciation was estimated according to other geomorpological studies (i.e., Baroni and Carton, 1991; Baroni et al., 2003). Sampling sites (soils) were chosen from an existing soil cartography study and soil inventory, based also on the evaluation of aerial photographs and on the results from past investigations (e.g., Sartori et al., 1997, 2004, 2005; Baroni et al., 2003; Egli et al., 2006). Boulders for SED dating were chosen directly in the field according to their position relative to the moraine, their shape and their stability. Boulders were chosen as near as possible to the investigated soils as to have an age-reference for the glacier extension and for soil ^{14}C dating. The soils S1, S2 and S5 developed near the treeline inside the north-east facing glacial cirque defined by Monte le

Pozze e Cima Tremenesca. S3 and S4 developed at 2370 and 2380 m asl, respectively, on a north-west facing Preboreal-estimated morainic sediment in the southern part of the same glacial cirque. S6 and S7 can be found in the north-facing side of the morainic sediments on which S1, S2 and S5 developed. S8 and S9 are located in the eastern part of the transfluence pass (Passo Cercèn) at the foot of a presumed inactive rockglacier and on the ridge of a recessional moraine (end Egesen-estimated), respectively. Boulder B1 is located on the distal side of a lateral moraine along the west side of the Monte le Pozze-Cima Tremenesca cirque in close proximity to soil sampling sites S1, S2 and S5. Boulder B2 is on the crest of an estimated-Egesen lateral moraine along the south-east side of the same cirque. Boulders B3 and B4 were probably transported to their present position by long-term permafrost/rockglacier creep in the small glacial cirque south-west from Cima Tremenesca. B5 is located on a different lateral moraine at a slightly higher elevation than B2. Boulders B6 and B7 are found in the cirque eastern of Passo Cercen. B6 is at the foot of a rockglacier where soil S8 is also located; B7 is on a frontal (recessional?) moraine ridge close to soil S9, while B8 and B9 (both rock outcrops in a small cirque, west-facing) are below the former transfluence pass (Passo Cercèn). B10 is located south of the ridge line below Monte Le Pozze, close to a lateral morainic sediment in the south-facing side of the investigated area.

1.7 Pre-historic human settlements and the use of fire

The first modern human inhabitants of Europe moved in from the Near East in the upper Palaeolithic era, approximately 45,000 years ago (Mellars, 1992), ultimately replacing the resident Neanderthals a little more than 30,000 years ago (Stringer, 1989). They came to occupy a large portion of the continent, but probably had to withdraw into a few warmer areas, or glacial refugees, during the coldest periods of the last glaciation, some 20,000 years ago, from which they may have re-expanded during the Lateglacial, Mesolithic period. Studies of human remains (teeth and bones) dated the first modern-human settlements in the Trentino region back to 14,000 years ago (Di Benedetto et al., 2000). Several pieces of evidence show that complex societies in the Trentino region have been present since the Mesolithic period (ca. 8000 – 4500 cal BP) (e.g., Cucina et al., 1999; Schmidl et al., 2005; Valsecchi et al., 2006). Archaeological studies show that European valleys and passes were already used frequently at the beginning of the Neolithic period (ca. 4500 cal BP). Humans have had a great impact on the natural landscape evolution and one of the most used tools has been fire. The hominid fossil record suggests that the routine domestic use of fire began around 50,000–100,000 years ago (Bar-Yosef, 2002) and the use of fire for managing plants and wildlife around 10,000 years ago (Pyne, 2001). Palaeoenvironmental studies in northern and southern Europe have shown that slash-and-burn agriculture has been an important cultivation

method since the Neolithic (e.g., Iversen, 1949; Pons and Thinon, 1987; Berglund, 1991; Carcaillet, 1998; Eckmeier et al., 2007). Artefacts documenting agricultural activities are dated in the Alps to around 7000 years ago or less (Bisi et al., 1987), so these remains span the time when agriculture spread into this region.

The importance of human settlements in this research work is linked to the impact the human society had (and still has) on land use and on landscape evolution by the use of fires.

Climate is the prime factor in driving large regional fires via antecedent wet periods that create substantial herbaceous fuel or drought and warming that extent conducive fire weather. Regardless, human activities and human-induced fires at the forest- and tree lines in the Alps have occurred for thousands of years (Whelan, 1995; Carcaillet, 1998, 2007).

Macrofossil charcoal is a term used to describe C-enriched, N-depleted pyrogenic organic plant material (fragments > 2mm in diameter), with a highly aromatic structure, which usually remain on the site of fire or immediately nearby, preserved through the process of incomplete burning (Schweingruber, 1978; 1990; Lynch et al., 2004; DeLuca and Aplet, 2008). Charcoal is a particularly useful record for the identification of fossil wood because the level of preservation is often good enough to examine the transversal, longitudinal and tangential wood sections and thus, through the observation of the wood structure, to identify the tree from which the charcoal derived to the genus (and in some cases to the species) level. Charcoal fragments allow the reconstruction of Lateglacial and Holocene landscapes and environments and the identification of fire events, changes in the vegetation, timing of soil development and changes in the land use (forests, pastures, charcoal piles, agricultural practises) (Carcaillet, 2000; Figueiral and Mosbrugger, 2000; Favilli et al., 2010).

2. Objectives

The investigation focuses on dating selected Alpine sites of distinct landform surfaces with several absolute and relative dating techniques in order to establish an absolute chronology of events and to correlate the information coming from the dating techniques used. The starting point was fixed at soils as indicators of landscape history. Soil has always been addressed as one of the most difficult materials to date using the radiocarbon technique (Matthews, 1985). The ^{14}C dating of a bulk soil does not give useful information about the age of a soil itself, but only about the apparent turnover time of Soil Organic Matter (SOM). The use of soils as indicators of landscape change needs an extraction method for the oldest pool of the SOM which could then be dated by means of ^{14}C, and gives indications about the duration of soil development.
We started from the basic assumptions that the first OM to form after glacier retreat is part of the most resistant OM pool, and that a chemical oxidation could mimic a natural microbial mineralization in order to remove the young and active fraction from the total SOM.

The research questions for the first part of this work were (*Manuscript I*):

a) Which chemical treatment is the most appropriate for the extraction of the oldest pool of the SOM?
b) How can the oldest OM compounds be characterised?
c) Which are the most important factors of OM stabilisation in Alpine soils?
d) Can the obtained ages contribute to the chronology of landscape evolution in the Holocene/Late Pleistocene?

The obtained ^{14}C ages were compared with results from relative techniques and with ^{10}Be (SED) applied on erratic boulders transported into the morainic sediment or by rockglaciers. The surface exposure dating (SED) using ^{10}Be is a reliable numerical dating technique providing information on the disintegration of the ice stream network at high elevations (see paragraph 1.5.2).
The chemical and physical characteristics of a soil open useful windows to relatively differentiate the surfaces and the natural processes which occurred during soil formation. The selection of suitable relative and absolute dating techniques is crucial for the establishment of an exact chronology of events and processes which occurred in every specific site.

The development of a new dating technique gave rise to additional research questions (*Manuscripts II-III*) :

a) Are numerical dating techniques, applied on different targets, comparable? What could be the reason for any differences?
b) Are relative dating techniques, such as soil evolution and weathering indices, in agreement with the numerical methods?

The study of charcoal fragments and of soil evolution has enabled a deepened understanding of the natural (and human-driven) events occurred in the investigated area throughout the millennia of its evolution. This part of the investigation has connected the natural Lateglacial landscape evolution to the more recent land-use modifications, mostly brought about by man. This part of the work has focused on the study of fire as one of the most often used tools by human societies to modify the natural environment (i.e. for pasture opening, cleaning-up for agriculture).

Consequently, we had the following research questions (*Manuscript IV*):

a) Can charcoal fragments be used as indicators of the soil age?
b) Can we determine the sources of the charred material?
c) What evidence do we need to relate the fire regime to the human impact on vegetation and land use?
d) Can charcoal be used for the reconstruction of the vegetation history?
e) What are the periods of higher human impact and how can they be recognised?

3. Summary of materials and methods

The present section provides a description of the methodologies used in the thesis; results are summarised in the following chapter.

3.1 Development of a methodology to date Alpine soils on a siliceous parent material (*Manuscript I*)

The first investigation was conducted with the aim to isolate the most stable pool of the organic matter and to obtain an organic residue which could then be dated with ^{14}C as a proxy for the timing of soil development. Two well-defined soil profiles, classified as *Entic Podzol (skeletic)* (IUSS Working Group, 2006), developed at 2100 m asl and at 2083 m asl on a supposed Oldest Dryas / Younger Dryas moraine(s) in the north-eastern part of Monte le Pozze were selected (Fig. 1.8 and 3.1). The soils were chosen on two different portions of the same slope as to detect possible different timing of moraine deposition. The morainic material was well stabilised by the presence of arboreal and bush vegetation and was sediment-rich; the soils developed below a natural forest of *Larix decidua* and *Juniperus* spp. The high vegetation cover and the tree development made the moraine very stable and the soils did not present any signs of erosion or burial. The first visual investigation of the soil profiles allowed us to estimate an undisturbed development from the beginning of soil formation and a high stability of the surface. The physical characterisation (*Table 3a*) has proved the high weathering under which these soils developed and the absence of a coarse material enrichment due to slope instabilities. In order to mimic natural OM microbial oxidation, we tested five chemical methodologies for the extraction of the most stable organic matter from the two studied soils (Table 3.1). We compared the technique according to Mikutta et al. (2006), in which NaOCl and HF were used to that according to Eusterhues et al. (2005) and Plante et al. (2004), in which H_2O_2 was used. The third conceptual approach hypothesised that a changed order of treatments, with HF as a first step, could liberate more organic C (destruction of organo-minerals associations) which would be oxidised in a second step by NaOCl. This procedure should have left behind an older organic C fraction. In an additional experiment, we substituted HF by Aqua Regia (3 volumes of HCl 32% + 1 volume of HNO_3 65%).

The organic matter functional groups of the soil residues at the end of the experiment were analysed by means of Fourier Transformed Infrared Spectroscopy (MIR-DRIFT). Complementary information was obtained by Scanning Electron Microscope (SEM) and Energy-Dispersive Spectroscopy (EDS) (Table 3.2). Furthermore, charcoal fragments found in the soil Lax 1 (S5) were

radiocarbon dated and used as an age reference for the ages obtained by radiocarbon dating of the organic residues after the different treatments.

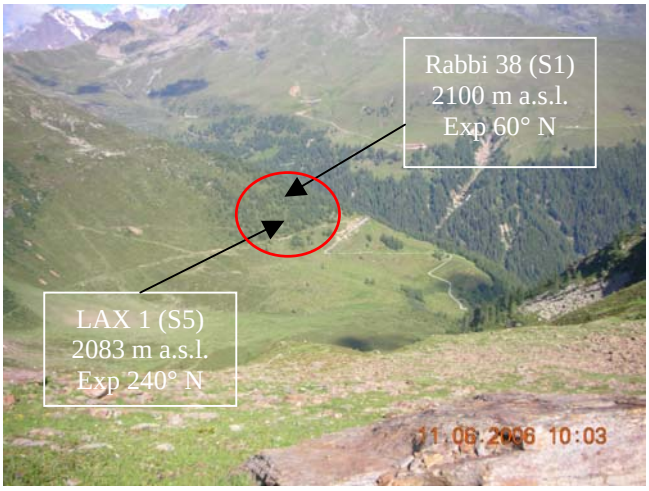

Fig. 3.1. Location of the two investigated soils

Tab. 3.1 Methodology for the extraction of the resilient pool of the organic matter

	Method 1	*Method 2*	*Method 3*	*Method 4*	*Method 5*
Step 1	10% NaOCl	10% NaOCl	10% HF	1 M Aqua Regia	10% H_2O_2
Step 2	10% HF	1 M Aqua Regia	10% NaOCl	10% NaOCl	-

Tab. 3.2 Methods used for soil chemical characterisation and radiocarbon dating (*Manuscript I*)

Carbon, Nitrogen	Elemental analysis (Elementar Vario EL)
pH	0.01 M $CaCl_2$
Particle size distribution	Sieving, X-ray sedimentometer (SediGraph 5100)
Charcoal in soil	Hand picked from soil; identification by stereomicroscope and reflected-light microscope
Dithionite, oxalate extraction	Extraction according to McKeague et al. (1971); analysis using AAS (Atomic Absorption Spectrometry – AAnalyst 700, Perkin Elmer, USA)
Functional groups, OM compounds	Mid infrared-Fourier Transformed infrared spectroscopy (MIR-DRIFT) (Bruker, Tensor 27)
Micrographs of treated samples	Scanning electron microscope (SED) and energy-dispersive spectroscopy (EDS)
Radiocarbon dating	Accelerator mass spectrometry (AMS) ^{14}C (ETH Zurich)

3.2 Application of the methodology for radiocarbon dating of resilient organic matter in Alpine soils in combination with Surface Exposure Dating of rock boulders with ^{10}Be (*Manuscript II*)

The methodology developed for radiocarbon dating of Alpine soils (*Manuscript I*) was applied in the investigated area to other soils in order to test the ^{14}C reliability and to try to reconstruct palaeoclimatic oscillations and glacier fluctuations during the late Pleistocene. Four soils (S1-S4; Fig. 1.8 and 3.2) developed inside the same glacial cirque at different altitudes and on different boulder-rich moraines were chemically characterised by means of their degree of podzolisation (translocation of Fe and Al phases in the B horizon) and treated with 10% H_2O_2 for the isolation of the oldest SOM fraction. Furthermore, the organic residues were radiocarbon dated. The radiocarbon ages were compared with the cosmogenic ^{10}Be SED ages of four boulders (B1-B4) located near the investigated soils. The selected boulders were located at similar altitudes and chosen, as much as possible, lying on the crest or on the distal part of a moraine, in a stable and flat position in order to avoid any long-term effect from slope-movement processes (Fig. 3.3A, B). Quartz samples were collected with a hammer and chisel from the flat tops of the boulders (Fig. 3.3C, D; Ivy-Ochs et al., 2004).

Tab. 3.3 Methods used for comparing radiocarbon dating with exposure dating (*Manuscript II*)

Carbon, Nitrogen	Elemental analysis (Elementar Vario EL)
pH	0.01 M $CaCl_2$
Particle size distribution	Sieving, X-ray sedimentometer (SediGraph 5100)
Dithionite, oxalate extraction	Extraction according to McKeague et al. (1971); analysis using AAS (Atomic Absorption Spectrometry – AAnalyst 700, Perkin Elmer, USA)
Extraction of resilient OM	10% H_2O_2, 168h, 50°C (Manuscript I)
Radiocarbon dating	Accelerator mass spectrometry (AMS) ^{14}C (ETH Zurich)
Exposure dating (^{10}Be)	Quartz extraction according to Ivy-Ochs et al., (1996); dating by Accelerator mass spectrometry (AMS) ^{10}Be (ETH Zurich)

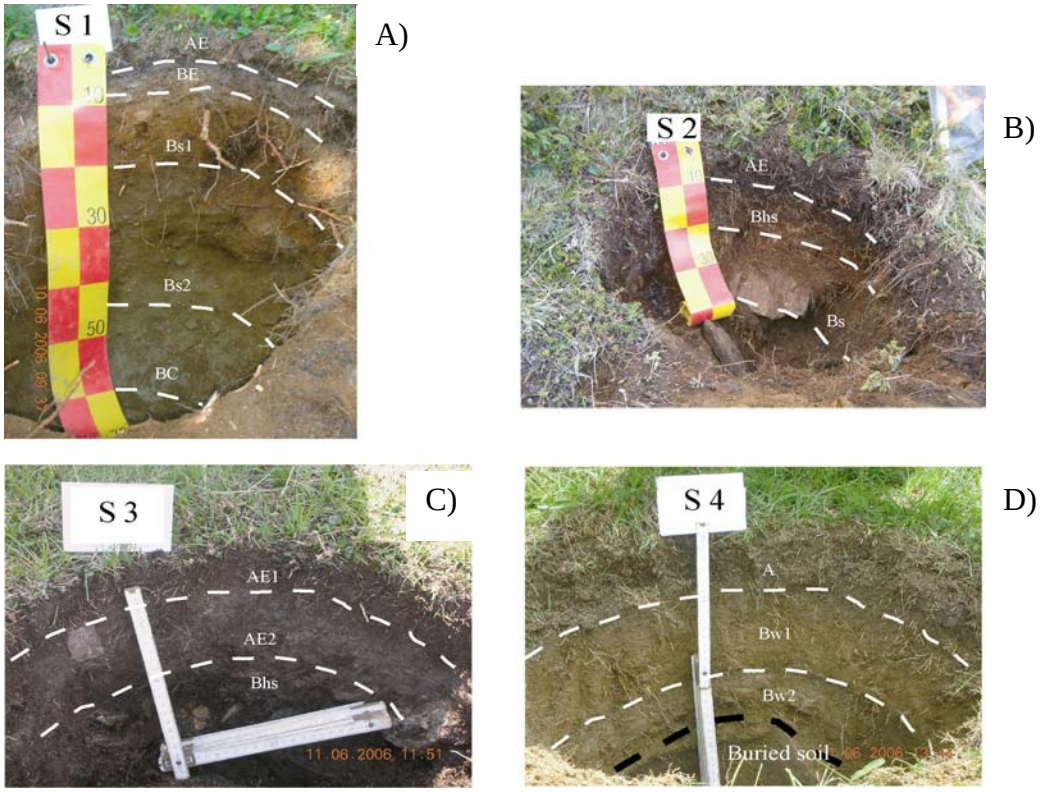

Fig. 3.2. Soils studied in *Manuscript II*. A) Entic Podzol (Skeletic) located at 2100 m asl; B) Haplic Podzol at 2230 m asl; C) Protospodic Leptosol at 2380 m asl; D) Brunic Regosol al 2370 m asl with indication of the buried horizons.

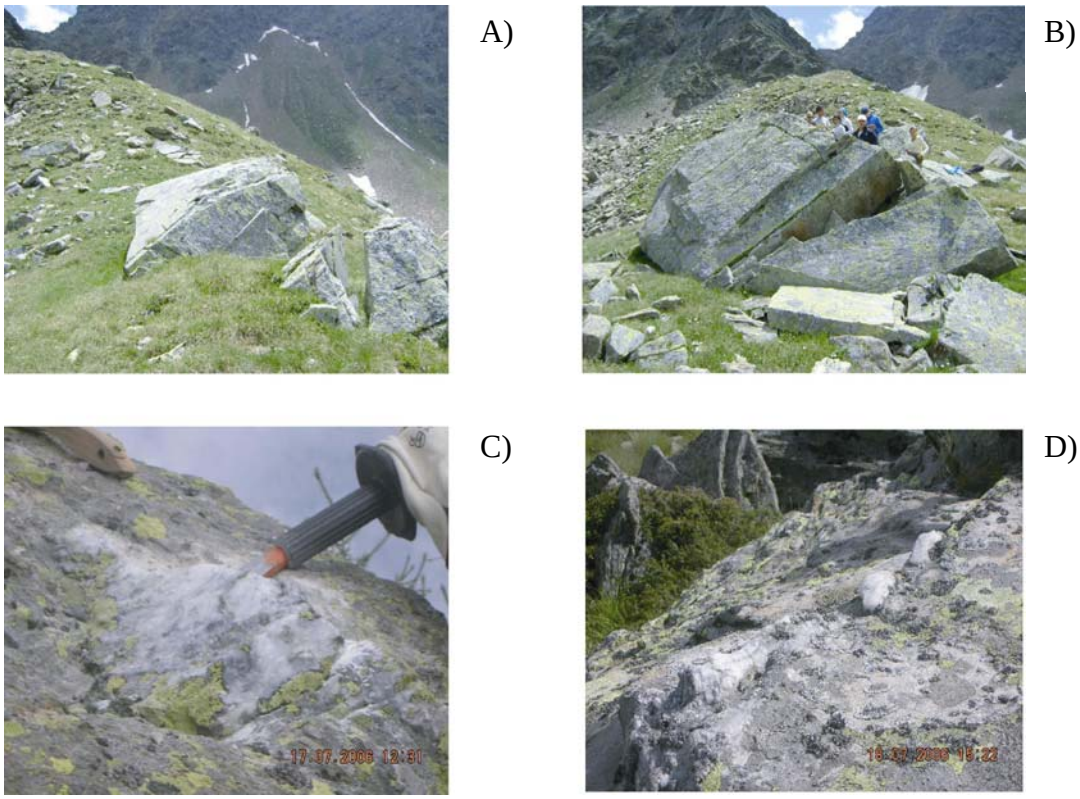

Fig. 3.3. A) Boulder B3 located at 2456 m asl; B) Boulder B4 located at 2446 m asl; C) Hammer and chisel to remove quartz vein from boulder B1; D) Quartz vein in boulder B2.

3.3 Combined application of relative and numerical dating techniques (*Manuscript III*)

We enlarged the area of application of the dating techniques to 9 soils and 10 boulders located on different morainic sediments which were estimated to be deposited between the Oldest Dryas and the Younger Dryas/Boreal chronozone. Our aim was to reconstruct the chronology of the deglaciation, to cross-check the results obtained from the different methodologies and to detect signals of occurred slope processes. The degree of podzolisation, clay minerals and mass balances were investigated for each site. The resilient fraction of the soil organic matter was extracted using 10% H_2O_2 (*Manuscript I*) and radiocarbon dated. Ten boulders in the proximity of the investigated soils were dated using cosmogenic ^{10}Be (SED) and used as an age reference. Some charcoal fragments extracted from one of the most developed soils were identified and radiocarbon dated in order to compare the obtained ages with those of the resilient OM (Table 3.4). This work (Favilli et al., 2009b) was intended to be a continuation of the methodological investigation started with Favilli et al. (2008).

Tab. 3.4 Methods used for comparing relative and numerical dating techniques (*Manuscript III*)

Carbon, Nitrogen	Elemental analysis (Elementar Vario EL)
pH	0.01 M $CaCl_2$
Particle size distribution	Sieving, X-ray sedimentometer (SediGraph 5100)
Dithionite, oxalate extraction	Extraction according to McKeague et al. (1971); analysis using AAS (Atomic Absorption Spectrometry – AAnalyst 700, Perkin Elmer, USA)
Clay minerals identification	Sedimentation (Carnicelli et al., 1997), X-ray diffraction
Mass balance	Method revised by revised by Egli and Fitze (2000); calculation using immobile element (Ti)
Charcoal identification	Hand picked from soil; identification by stereomicroscope and reflected-light microscope
Extraction of resilient OM	10% H_2O_2, 168h, 50°C (Manuscript I)
Radiocarbon dating	Accelerator mass spectrometry (AMS) ^{14}C (ETH Zurich)
Exposure dating (^{10}Be)	Quartz extraction according to Ivy-Ochs et al., (1996); dating by Accelerator mass spectrometry (AMS) ^{10}Be (ETH Zurich)

3.4 Charcoal fragments as contemporary evidence of landscape evolution during the Holocene (*Manuscript IV*)

In this study we investigated the fire regimes and the vegetation succession by means of charcoal fragments extracted from nine Alpine soils (Table 3.6). The charcoal identified fragments (Fig. 3.4) were divided further at the genus level using a reflected-light microscope (objective 5x, 10x, and 20x, Olympus BX 51, Japan). The observations were compared with a histological wood-anatomical atlas, using an identification key (Schweingruber, 1990).

Tab. 3.6 Methods used for soil analysis and charcoal identification and dating (*Manuscript IV*)

Carbon, nitrogen	Elemental analysis (Elementar Vario EL)
pH	0.01 M $CaCl_2$
Oxalate extraction	Extraction according to McKeague et al. (1971); analysis using AAS (Atomic Absorption Spectrometry – AAnalyst 700, Perkin Elmer, USA)
Charcoal identification	Hand picked from soil; identification by stereomicroscope and reflected-light microscope
Radiocarbon dating	Accelerator mass spectrometry (AMS) ^{14}C (ETH Zurich)

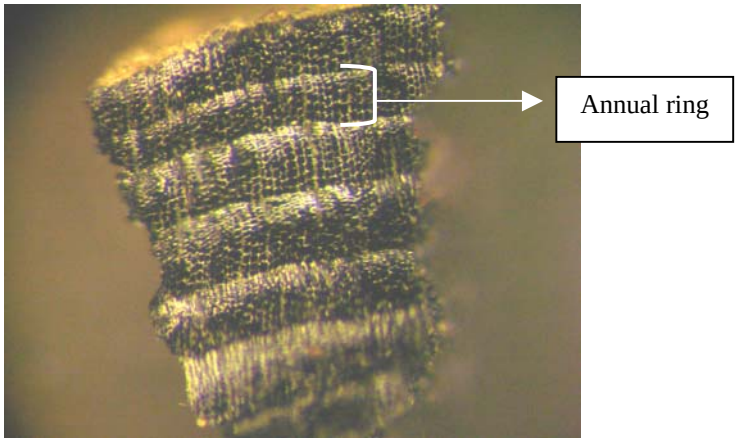

Fig. 3.4. Photograph of charcoal fragment of *Larix decidua* under stereomicroscope with indication of tree rings.

4. Synthesis

The synthesis summarises the results that can be found in the manuscripts (Part B) and gives a general conclusion.

4.1 Results

4.1.1 Comparison of different methods of obtaining a resilient organic matter fraction in Alpine soils. (Manuscript I)

The two investigated soils Rabbi 38 (S1) and Lax 1 (S5) were well developed and had a bleached horizon (AE) followed by a horizon with accumulation of sesquioxides (Bs). They showed a typical eluviation and illuviation of Fe and Al, presented a high proportion of soil skeleton in the subsoil and a loamy-sand texture. The chemical and physical characterisation confirmed that both soils underwent an undisturbed development (*Tables 3a* and *4*).

The five methods we used to extract the OM fractions were the following:

1. 10% NaOCl + 10% HF
2. 10% NaOCl + 1M Aqua Regia
3. 10% HF + 10% NaOCl
4. 1M Aqua Regia + 10% NaOCl
5. 10% H_2O_2

Methods 1 to 4 allowed 3 OM fractions (*Labile*, *Intermediate* and *Resilient* OM) to be distinguished. With method 5 only 2 OM fractions could be isolated (*Labile* and *Resilient* OM).

Method 1 and 2, with HF and Aqua Regia as a second step, led to very small differences with respect to the OM fractions (see *Manuscript I*). Compared to Aqua Regia, HF caused a higher loss in weight of the samples, because of the solubilisation of silicates (e.g., kaolinite – Fig. 4.1A). HF had also a bigger effect on nitrogen compared to carbon compounds (Schmidt and Gleixner, 2005; Eusterhues et al., 2007). DRIFT analyses have shown the formation of cryoliote (Na_3AlF_6) (Alghen et al., 1999) in the residues after the HF treatment (Fig. 4.1B). The formation of cryolite probably could have caused the precipitation of young OM, which influenced the radiocarbon age of the resilient OM. Contrary to our hypotheses, both methods with HF (1 and 3) led to the youngest ^{14}C ages of the resilient fraction (~9000 cal BP). Aqua Regia (methods 2 and 4) was efficient in eliminating organic matter (65-70%) and isolating a resilient old C fraction (~11,000 cal BP). The H_2O_2 treatment (method 5) led to a strong oxidation of SOM (up to the 90%) and left behind a very old OM fraction (~17,000 cal BP). This age is consistent with a possible glacier readvance during the Oldest Dryas (Ivy-Ochs et al., 2008) in the investigated area. The ^{14}C ages of resilient OM

increased in the following order: untreated samples < method 3 (HF+NaOCl) ≤ method 1 (NaOCl + HF) ≈ method 2 (NaOCl + Aqua Regia) < method 4 (Aqua Regia + NaOCl) < method 5 (H_2O_2). With H_2O_2, the oldest ages of both soils were found in the uppermost horizons (*Table 5a*). DRIFT analyses have shown that the H_2O_2-oxidation-resistant organic fraction was enriched in N-containing, aromatic and aliphatic compounds (Fig. 4.1C). The ^{14}C ages of the charcoal fragments indicated that a fire event occurred at the beginning of the Holocene (ca. 10,400 years ago) in a *Larix decidua* forest. This forest developed on the soil formed on the sediments that were deposited during the Younger Dryas (Fig. 4.2). The resilient fraction after the H_2O_2 treatment did not show any correlation with the soil properties and components (e.g., clay fraction). This result was confirmed also by other authors (e.g., Helfrich et al., 2007). H_2O_2 removed an easily degradable and labile fraction leaving behind a refractory organic material. N-containing compounds were less affected by oxidation probably due to their absorption on minerals.

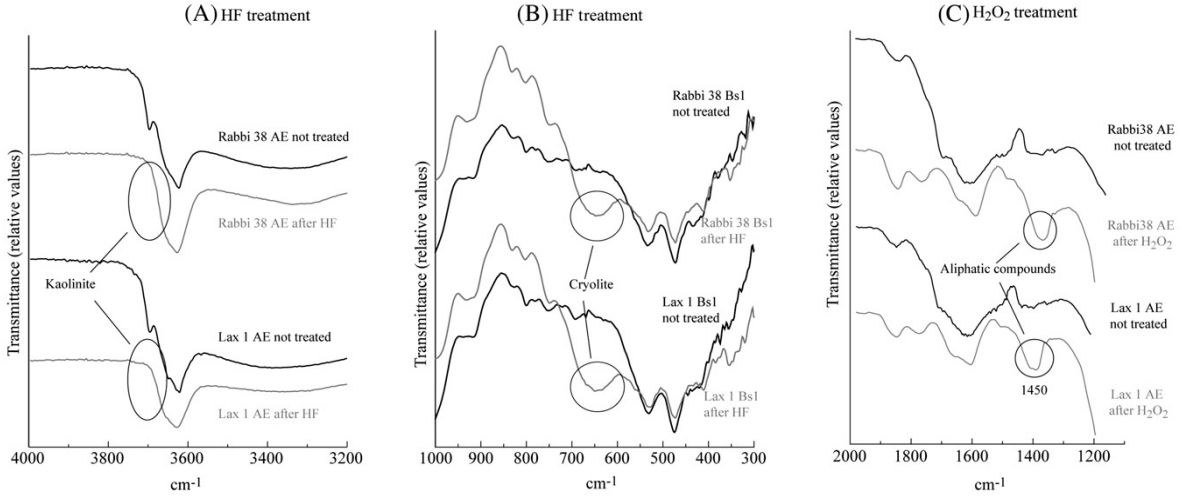

Fig. 4.1 Comparison of DRIFT spectra before any treatment and (A and B) after the HF treatment (method 1) and (C) after the H_2O_2 treatment (method 5). It is noticeable the solubilisation of the silicates (A) and the formation of cryolite after the HF treatment (B) and the enrichment in aliphatic compounds after the H_2O_2 treatment (C). From *Manuscript I.*

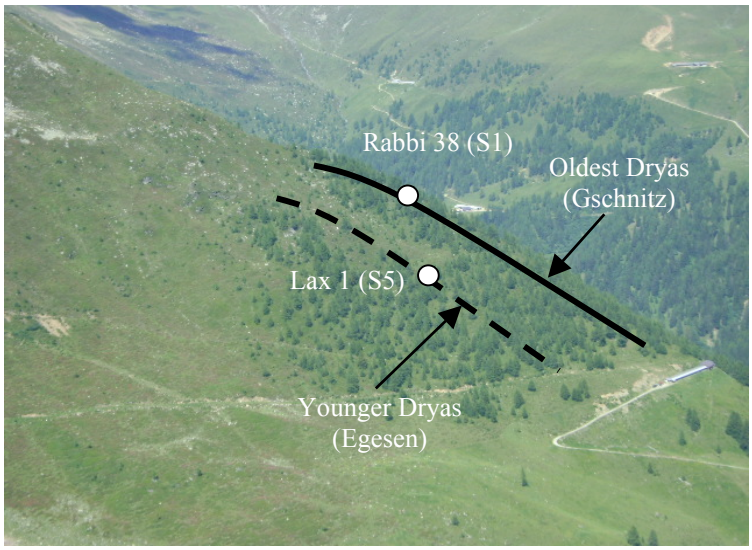

Fig. 4.2.
Larix decidua Mill. natural forest with the indication of the two possible deposition phases.

4.1.2 Combination of numerical dating techniques using ^{10}Be in rock boulders and ^{14}C in resilient soil organic matter for reconstructing glacial and periglacial processes in a high Alpine catchment during the late Pleistocene and early Holocene. (Manuscript II)

The four investigated soils showed a typical evolution towards a Podzol development. The most advanced ones (S1 and S2) developed at 2100-2200 m asl near the timberline on a moraine with an assumed Younger Dryas age on the north-east facing glacial cirque north of Monte le Pozze (Fig. 1.8 and 3.2). The relationship between the ^{14}C data of the resilient organic matter and the ^{10}Be ages with altitude was found to be significant and could explain the glaciers' possible retreat in this small catchment between 17,000 and 9000 years ago (Figs. 4.3).

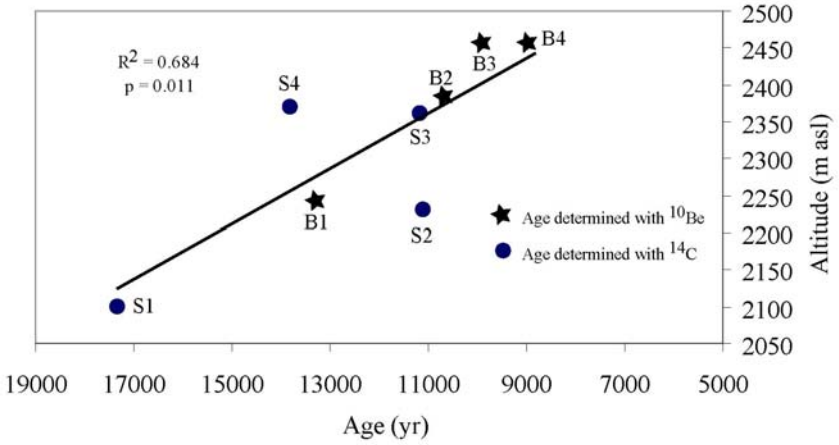

Fig. 4.3 Relationship between the obtained ages (^{14}C [calibrated ages] and ^{10}Be) and the elevation of the dated objects.
(Modified from *Manuscript II)*.

The soils S3 and S4 (Fig. 1.8, 3.2C, D and 4.4), although very close to each other, showed a different evolution. The soil S3 developed on a north-facing moraine (^{10}Be age of B2 and ^{14}C age of stable OM of S3 – *Tables 2* and *5a*). This soil showed the typical characteristics of a developing Podzol and evidence of an undisturbed evolution. Soil profile S4 did not show a clear translocation of Fe and Al, due to a lower stage of soil development. This soil was found to be polygenetic (Fig. 3.2D) because it developed in an area with former solifluidal activity. The oldest pool of the OM in the top buried horizon (Ab) revealed a maximum age of OM formation (13,596 – 13,991 cal BP) that falls into the Bølling-Allerød warm phase. Due to the steep slope on the west side of the soil S4 and to the great lobes accumulation on the east side of it, the sediment on which S3 developed was probably deposited by a push moraine (Haeberli, 1979) (Fig. 4.4 and paragraph 4.4). The polygenetic horizon sequence of S4 was due to the accumulation of younger material (~8500 cal BP) on top of a former, older surface. The concentration of organic C in the profile S4 showed a strong increase in the Ab horizon, thus confirming the macromorphological observation (*Tables 3a* and *4*). The ^{14}C dating of roots residues found in the Ab horizon allowed us to estimate the timing

of burial, which was found to have occurred in the Göschener I cold phase around 3000 years ago, when new periglacial activities were stimulated.

Fig. 4.4. Location of the investigated soils S3 and S4 and multi-lobed sediment deposition (push moraine) during the Younger Dryas readvance phase. (Photo by Wilfried Haeberli).

4.1.3 Combined use of relative and numerical dating techniques for detecting signals of Alpine landscape evolution during the late Pleistocene and early Holocene. (Manuscript III)

This manuscript presents the continuation of the investigation methodology based on the combined use of different dating techniques giving a general conclusion about the applied methodology and the landscape evolution of the investigated sites. The results obtained from this study showed a fairly good agreement among the different dating techniques. In four of the nine studied soils, the oldest OM ages were found in the topsoil (*Table 5a*). The ^{10}Be ages of the boulders located near the studied soils were comparable to the ^{14}C ages of the soils (*Table 2*). The radiocarbon dating of the SOM-stable fraction of the investigated soils and the ^{10}Be ages of the boulders were related, respectively, with the warm and cold phases of the Lateglacial, and contribute to our knowledge of the duration of the different stadials in the investigated area (Fig. 4.5).

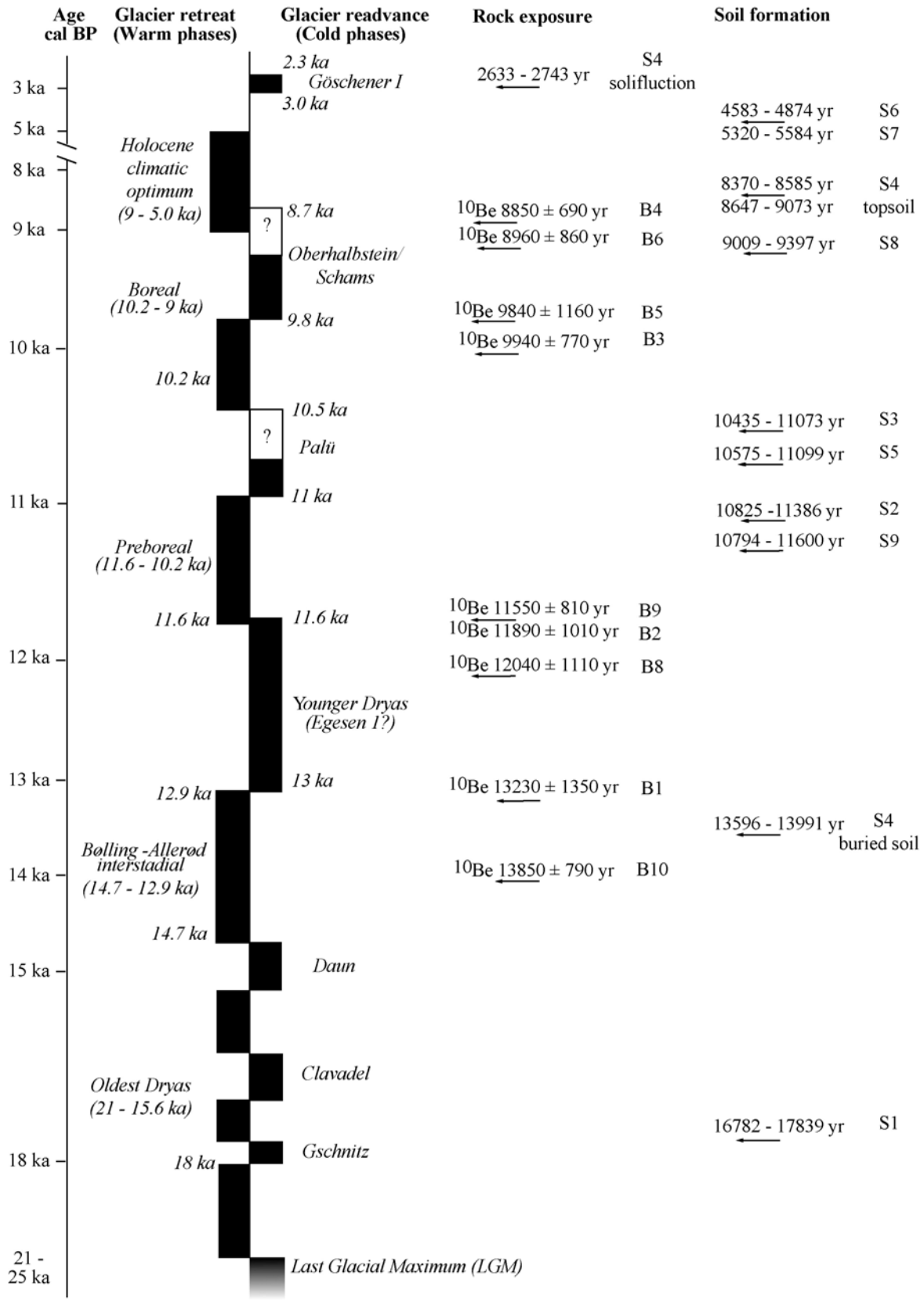

Fig.4.5. Absolute ages of the investigated sites related to the chronology of the Lateglacial and Holocene glacier and climate variations (from *Manuscript III* according to several authors, e.g., Maisch 1987; Maisch et al. 1999; Kerschner et al. 1999; Ivy-Ochs et al. 2004). Question marks (?) are used to indicate the uncertainties in the extension of the cold phases in the investigated area.

Relative dating, such as the development of typical podzolic features (difference in the content of pedogenic and poorly crystalline Al (ΔAl_o) between the spodic (Bs/Bhs) and the eluvial (E/AE) horizon), showed a direct relationship to the age of the resilient OM (resistant to H_2O_2) (Fig. 4.6).

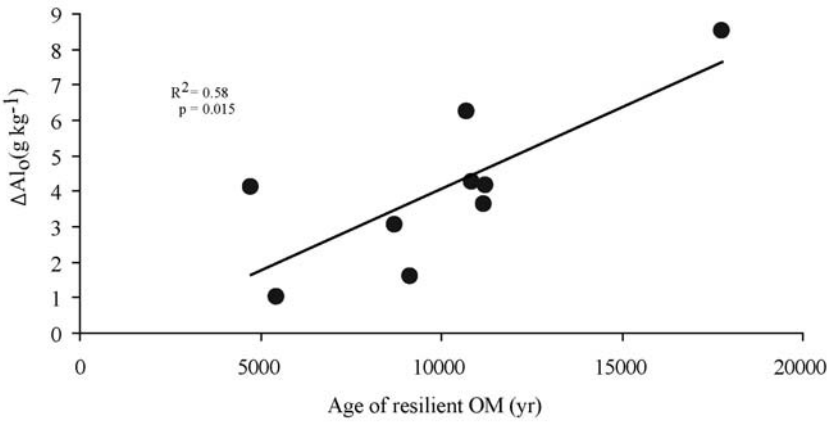

Fig. 4.6. Correlation between the content of pedogenic and poorly crystalline Al (Al_o) that migrated to the Bs1 (or Bhs) horizon (expressed as the difference of Al_o (B horizon) - Al_o (topsoil)) and the ^{14}C age of the resilient OM of the investigated soils. (*Manuscript III)*

The mass balance calculations showed that the oldest soils (^{14}C age of resilient OM) have lost up to 75% of their initial content of Si, Al, Fe and base cations (Na, Mg, Mn, K, Ca) in the top horizon (Fig. 4.7). Also in this case, the higher the elemental losses, the higher is the age of the resilient OM.

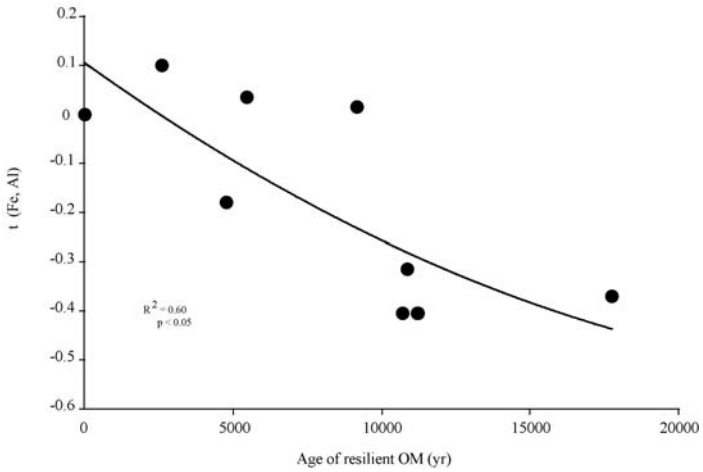

Fig. 4.7. Open system mass transport function $\tau_{j,w}$ as a function of the age of the soil profiles (^{14}C age) for the mean value of Fe + Al (*Manuscript III*).

4.1.4 Charcoal fragments of Alpine soils as indicator of landscape evolution during the Holocene in Val di Sole (Trentino, Italy). (Manuscript IV)

The identified species of charcoal fragments were similar to those which dominate the subalpine and Alpine forest today (in particular *Larix decidua, Picea abies, Clematis spp,* and *Ericaceae*). Some plant displacements through the centuries could be observed by the charcoal composition and age within the individual soil profiles (Fig. 4.8). The oldest charcoal fragments had an age of around 10,500 cal BP and were found in the deepest soil horizons, in accordance with the assumption of the stratification of wood charcoal in soil (the older, the deeper – Carcaillet, 2001). The charcoal fragments of the high-alpine soils confirmed the early Holocene establishment of the forest (*Larix decidua, Pinus sylvestris* and *Pinus mugo*). The charcoal fragments extracted from the soil at 2222 m asl revealed a downward shifting of the treeline by about 150 m from the early Holocene to the present-day situation (Favilli et al., 2010).

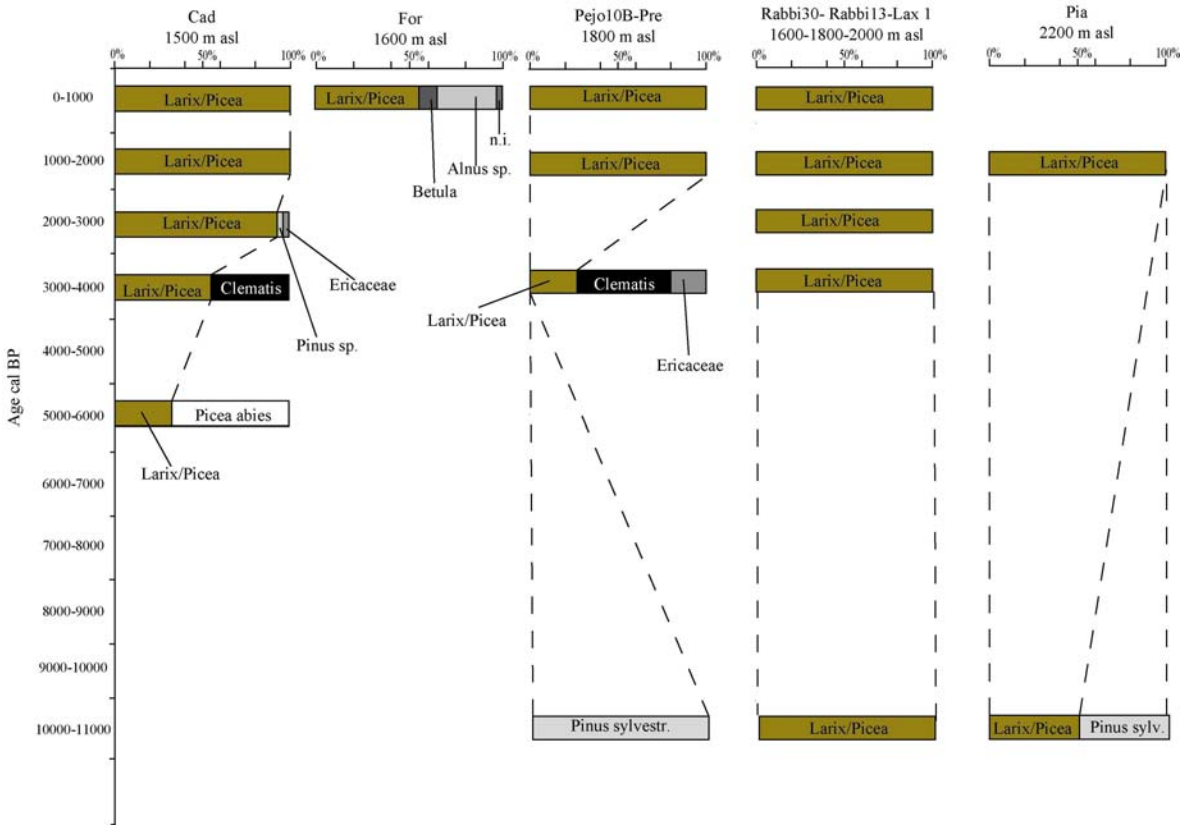

Fig. 4.8. Composition of the vegetation as a function of time derived from charcoal fragments in the soils (*Manuscript IV*). Some soils having a similar altitude and evolution were unified in one graph. n.i.= not identified

Charcoal dating also revealed a possible human impact on the natural territory since the Copper Age (around 3000 cal BC). The major part of the dated charcoal fragments fall into the Bronze Age (ca. 2200 – 1300 cal BC; Fig. 4.9), a period with an established human presence at very high impact because more complex societies had developed. At high altitudes, forests and meadows were used

as pastures. The charcoal fragments of the Bronze Age correlate well with the climate change that occurred around 3000 – 3500 BP and leading to the Göschener cold-phases (Zoller et al., 1966; Burga and Perret, 1998; Maisch et al. 1999).

The investigated area has been used for agro-forestry purposes up to present day. Thirteen fire events in the past 10,700 years were recognised, and seven of them can be attributed to human origin. According to the ^{14}C ages of the charcoal fragments, the greatest human impact in modern history in this area was recorded in the elevation range 1500 – 1800 m asl.

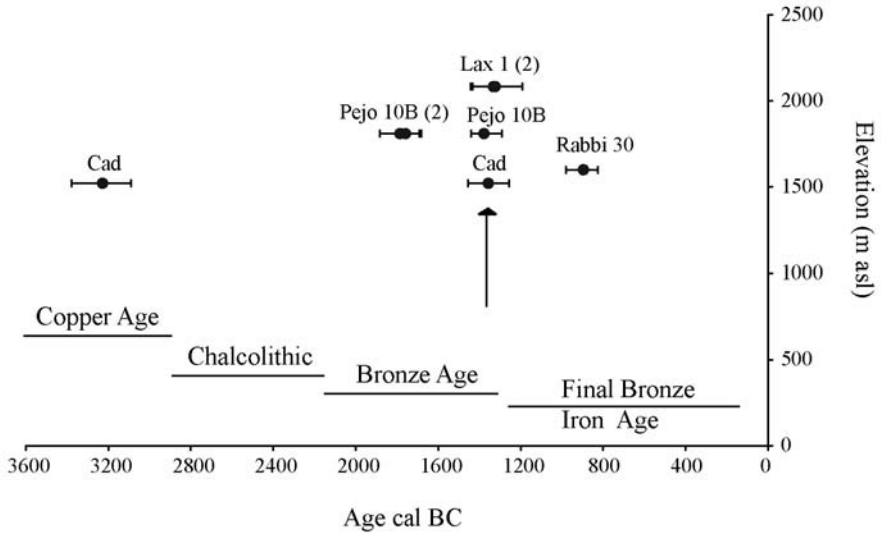

Fig. 4.9. Fire chronology between 3600 and 0 cal BC. The highest impact was detected during the Bronze Age. The arrow indicates a synchronous fire detected in different sites (*Manuscript IV*).

4.2 Discussion of the applied methodology (soil dating)

The present geochronological study has focused on the dating of sensitive sites in a relatively small area of the East Italian Alps. A big step forward has been made in the possibility of radiocarbon dating of Alpine soils, obtaining reliable ages despite some questions remaining unresolved. Considering that the attack of the weathering agents starts as soon as a sediment is exposed, and that soil development proceeds increasingly at greater depths, the location of the oldest OM pool in the top horizons seems to be logical. The first OM occupies all the available binding sites of the minerals and the continuous addition of OM does not completely displace the first OM pool. We obtained valuable insights into the composition of the OM stable pool and the major stabilisation mechanisms in Alpine soils. Aliphatic, aromatic, amide and nitrogen compounds seem to be part of the oldest OM pool. Their stabilisation in the soil matrix is mostly due to their intrinsic chemical characteristics, although the association between the soil clay fraction and the OM has been identified as one of the major stabilisation mechanisms. The reliability of the ^{14}C ages of the resilient pool of organic matter from an ice-free surface was tested comparing it with other age references, such as SED using cosmogenic ^{10}Be or the ^{14}C dating of charcoal fragments. The obtained ages (^{10}Be and ^{14}C) were directly comparable and showed that the first OM needs some

500-1000 years to be stabilised at these altitudes (2000 – 2600 m asl) (i.e., difference between the ^{10}Be age of boulder B2 and the ^{14}C age of soil S3). The extraction technique for the oldest SOM, based on 10% H_2O_2, seems to lose its oxidation efficiency when the soil horizon has more than 10% of organic carbon. The ages obtained from the dating of the resilient OM of such C-rich horizons are always younger than the ages expected. In these cases, we have to consider the relative position of the soil on the moraine with respect to other dated soils (or boulders) in the area and its chemical and physical characteristics. This, combined with relative dating, can avoid an incorrect interpretation of the ^{14}C ages. The ^{14}C dating of charcoal fragments is, furthermore, an important representative for the duration of soil formation and for vegetation changes due to climate and human forcing. The impact of human societies on the natural environment has been demonstrated by the detection of at least seven local human-induced fires during the last 6000 years.

The chemical and physical characteristics of Alpine soils are strictly bound to the time of soil development and can give invaluable insights about the reactivity of the Alpine environment. A soil keeps the memory of the events which occurred during its development and can be considered an archive. The mass balance approach has shown that the oldest soils have lost, in their uppermost horizons, up to 75% of the total amount of elements, compared to the least weathered horizon (BC/C horizon). These losses are directly comparable with the ^{14}C ages of the oldest organic matter. A distinct amount of secondary clay minerals was only found in the most weathered horizon of the oldest soils (> 8000 years – *Table 6*).

4.3 Landscape evolution of the studied sites in Val di Sole

The landscape of Val di Sole, as we can see it today, evolved – aside from the structures given by the geology and the tectonics – from the slow modifications induced by the movements of the glaciers and the subsequent retreat phases and periglacial activities. All dated objects and landforms refer to the period between the beginning of deglaciation (Oldest Dryas) and the Holocene climatic optimum (between the Boreal and the Older Atlanticum chronozones). The valleys up to the glacial cirques are covered by morainic material. The obtained ages and relative dating analyses confirmed our initial hypothesis; the Egesen readvance stadials (Younger Dryas chronozone) is one of the most clearly represented in the area and most of the sampled boulders referred to that period. Most of the studied soils started to develop after the Younger Dryas chronozone.

During the LGM the area was most probably completely covered by ice originating from the cirque Monte le Pozze-Cima Trenemesca and from the cirque delimited by Cima Vallon and Cima Grande. The first period of deglaciation, shortly after the glacier maximum extent, was probably fast (few centuries – Ivy-Ochs et al., 2008) and has probably left, as confirmed by our analyses, some local

glaciers or permafrost activity at the highest altitudes (> 2400 m asl). The glacial cirque delimited by Monte le Pozze and Cima Tremenesca has a sediment-rich moraine deposited during the readvance stadial after the first period of deglaciation (Oldest Dryas), as seen by the ^{14}C dating of soil S1. The soils S1, S2 and S5 were invested by different sediment deposits due to small glaciers forming in the cirque at the highest altitudes. The sediments from the top of the moraine were exposed at different times and reflect a sort of "chronosequence".

Although the oldest age of the resilient OM of soil S1 refers to the Oldest Dryas, no other soils were found with a similar age. For this reason, the obtained ages must be handled carefully. More research is needed to discover other moraines deposited during the Oldest Dryas readvance phases, in order to know the glaciers extension at that time in the investigated area.

During the Bølling-Allerød warm period, glaciers retreated up to ca. 2500 m asl on south-facing slopes (^{10}Be age of boulder B10) and up to ca. 2400 m asl on north-facing slopes. Soil S4 contains a buried soil which seems to have formed during the Bølling-Allerød warm period. It might, however, be that this soil was covered by ice (push moraine) during the Younger Dryas. The morphology and the ^{14}C – ^{10}Be ages of the sediment where soil S3 developed would support this hypothesis (cf. Haeberli, 1979). Basically, a discontinuous freezing process (permafrost formation) had transformed the sediment into cohesive material with reduced strength, allowing the formation of a multi-lobed deposition pushed on the side of the glacial cirque due to the stress exerted by the glacier. The stress transmission of the glacier was capable of deforming the frozen sediment and depositing it in the observed manner, avoiding a new deposition on the site of S4 (Fig. 4.4 and 4.10).

Evidence of a glacier-friendly climate during the Younger Dryas (Egesen stadial) are numerous in the investigated area. In the glacial cirque Monte le Pozze-Cima Tremenesca a glacial readvance during the Egesen stadial deposited new material which partially buried the former (Oldest Dryas). The Oldest Dryas sediment was found at an altitude of 2100 m asl but only in the topsoil of S1. The subsoil of S1 has an age referred to the end of the Egesen period, the same as the soil S5 and S2, located at 2083 and 2200 m asl respectively (Fig. 4.11).

Fig. 4.10. Location of S3 and B2 and indication of the possible deposition of the sediment (push moraine).

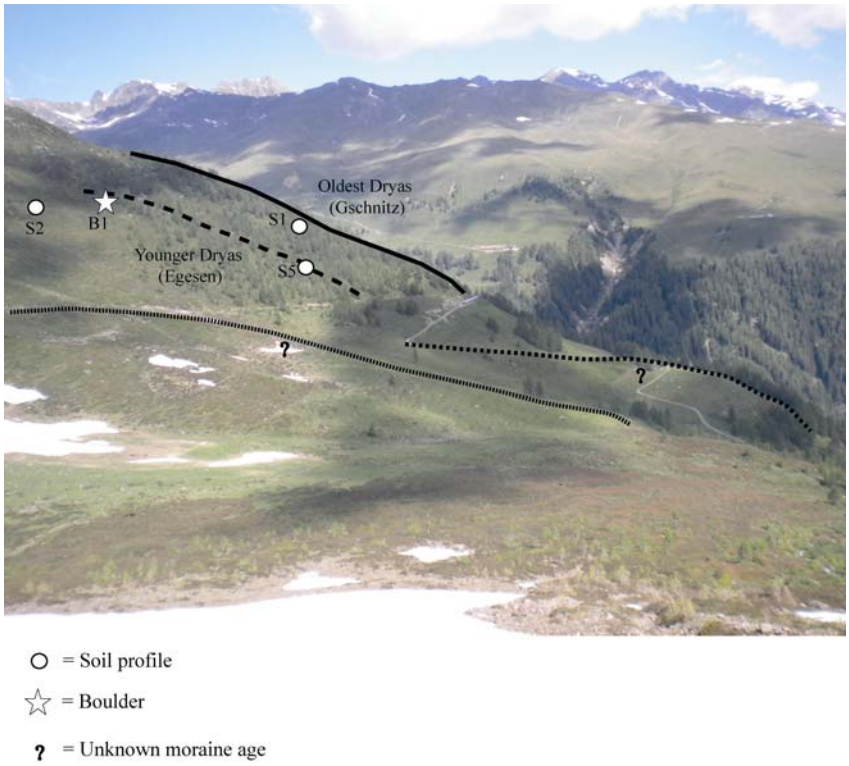

Fig. 4.11. Location of the soil profiles S1, S2, S5 and of the boulder B1 (north-east facing slope). Modified from *Manuscript III*.

The extension of the morainic deposition during the Egesen is represented by the boulder B1, by the soils S2 and S5 in the western part, by the soil S3 on north-facing slopes and by the soil S9 in the eastern part of the valley (Fig. 4.12). According to the obtained ages, the Egesen readvance phases began around 13,230 ± 1350 years ago (B1) and ended around 11,550 ± 810 years ago (B8, B2 and B9). The Egesen glaciers reached an altitudinal low of 2360 m asl on north-facing slopes and of 2586 in the eastern part (Passo Cercèn). The soils S2, S3, S5 and S9 show slightly younger ages (between 11,600 and 10,400 cal BP). This refers to the Preboreal warm phase. The dating of charcoal fragments extracted from the soils located above or just below the treeline have been dated back to the onset of the Holocene, around 10,500 years ago, demonstrating a quick afforestation at that period. One of these soils was located above the present treeline at 2222 m asl and demonstrates a downward shifting of the treeline from the Holocene period.

After the Preboreal, a glacier-friendly climate stimulated the readvance of small local glaciers and rockglaciers, only at the highest altitudes (> 2400-2500 m asl), contributing to the downward shifting of the treeline to the present position. During the cold phase in the Boreal chronozone (Oberhalbstein/Schams) the boulders B3, B4, B5 and B6 were deposited at c. 2500 m asl (average age c. 9500 years ago). The boulder B6, located at the foot of an inactive rockglacier, demonstrated that the east-facing part of the area was affected by permafrost activities around 9000 years ago at an altitude of c. 2600 m asl (Fig. 4.12). The same was detected at the sites of B3 and B4, which were most probably deposited due to permafrost/rockglacier activities. During the Holocene

climatic optimum (9.0 – 5.0 ka), the organic matter of soil S8 (2552 m asl), located near B6, was already formed and stabilised.

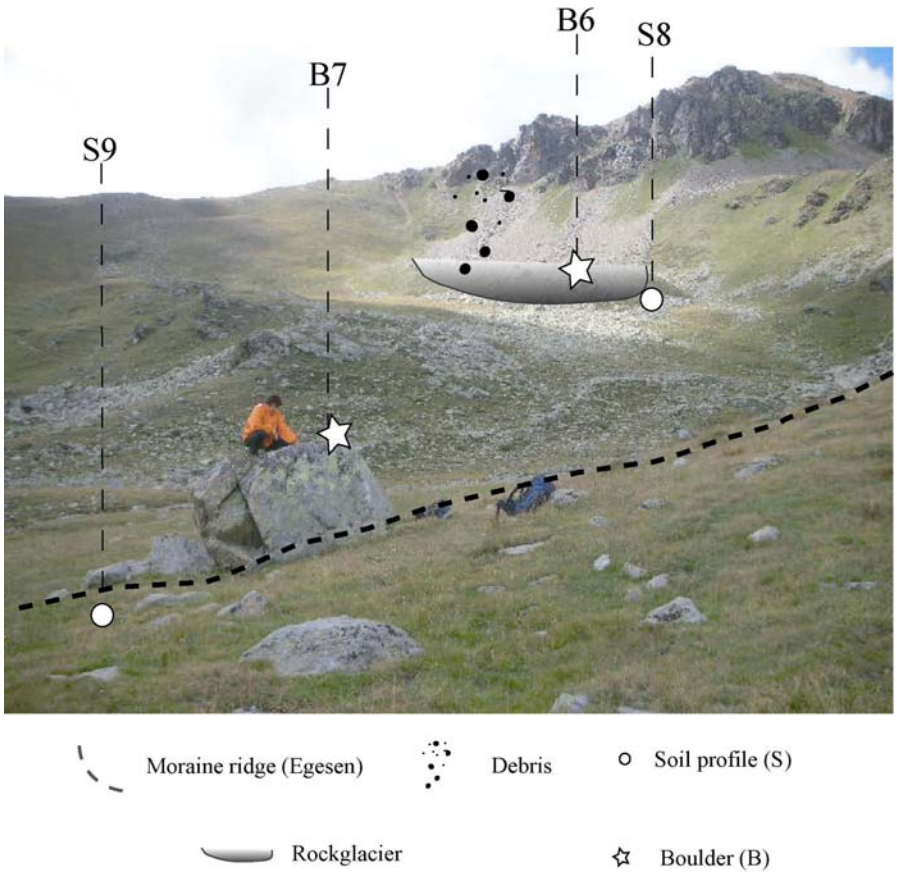

Fig. 4.12. Location of the profiles S8 and S9 and of the boulders B6 and B7 (east-facing slope).
Modified from *Manuscript III*.

According to our ages, the area was completely deglaciated at the onset of the Holocene climatic optimum. Local periglacial processes (permafrost, solifluction activities) have affected the north-facing cirque at c. 2400 m asl, around 3000 years ago, during the Göschener I cold phase, causing the burial of soil S4.

After these landscape modifications, man began to establish activities in these valleys and to affect the environment. The first human interference was recorded in the area around 3000 years ago, during the Copper age. The results of our study have shown that humans have modified the landscape of Val di Sole, Val di Pejo and Val di Rabbi continuously from their first establishment to present times. The dating of charcoal fragments has demonstrated the use of the fire as a tool for clearing the landscape for agricultural and trading purposes. Charcoal were often produced in holes excavated inside the forests, evidence of a tradition which persists until today (charcoal piles). According to our data, a quick forest expansion establishment phase must have occurred shortly after the Lateglacial around 10,500 cal BP, with the establishment of *Pinus sylvestris* and *Pinus mugo*. These species were slowly displaced by *Larix decidua* and *Picea abies* at the transition between the Boreal and the Atlantic (9000 – 7400 cal BP) chronozones. The lower altitudes sites

were used as pastures during the Bronze age and during the Roman period the agriculture changed towards a specialization in viticulture and lowlands activities. The last two centuries were characterized by an increased need for wood due to the development of iron smelting sites and, in the twentieth century, by the abandonment of the countryside and the progressive industrialisation of the region. This has contributed to an increase in afforestation and to a growing interest for the natural environment as a recreational resource. Today these valleys are intensively used for cultural and sports activities (tourism, skiing, trekking, rafting).

4.4. Implications

Geochronology:

The used dating techniques have revealed the deglaciation periods and the changes in vegetation of a part of Val di Sole (and related valleys) during the late Pleistocene and early Holocene. The combined use of relative and absolute dating methods has shown that an investigation carried on from different points of view, on different spatial and temporal scales, can detect crucial details and give an important contribution to the chronology of the Lateglacial. An enlarged understanding of this time span provided insights into the sensitivity of Alpine areas regarding fast changing environmental condition. More research is needed in order to test the reliability of the developed techniques at other Alpine sites.

Landscape evolution and weathering modelling:

The combined methodology is a powerful tool for dating surfaces. The ages obtained can be integrated in modelling landscape evolution in the late Pleistocene and early Holocene and also to make predictions about the reaction of Alpine landscapes to the global change. Chemical and physical data could be integrated in weathering modelling to understand the timing and the processes related to the Alpine soil formation in much more detail.

Soil Science:

The fate of soil organic matter and the stabilisation mechanisms, leading to the formation of an old carbon pool, are still not clear. The use of the podzolisation process as a relative dating technique provides important information about the soil formation, horizon differentiation and surface stability. The development of clay minerals and the calculation of mass balances in the soil gives further insights into the weathering effects.

Geomorphology:

The applied numerical dating techniques on geomorphological objects are useful tools to knowing the depositional time of moraines and boulders. Applied in combination with relative dating techniques, they help to decipher slope and periglacial processes. A combined methodology enables a mutual control and subsequently, a better interpretation of the timing of geomorphic features formation and helps in understanding the present landscape formation.

Geo-Archaeology:

The presence of charcoal fragments of different ages can be a good evidence of human impact on the natural territory from the pre-historical to modern times. The distribution of the fire patterns provides crucial indications about the fire dependency on climate shifting.

5. Perspectives

Following this investigation, several questions remain:

- What is the chemical composition of the H_2O_2-extracted organic matter pool and what are the main OM stabilisation processes occurring in Alpine soils?
Our investigation has revealed that the oldest organic matter pool is enriched in nitrogen, aliphatic and amide compounds. Furthermore, in four of nine soils, the oldest OM was detected in the topsoil. Possible perspectives could include the molecular investigation of the chemical composition of the H_2O_2-extracted organic matter pool more in detail in order to clarify what exactly is isolated by the oxidation technique.

- Is it possible to apply the developed dating methodology to Alpine soils on non-siliceous parent material? What would be the required modifications?

The identification and dating of charcoal fragments is a powerful technique to investigate past climatic variation, vegetation changes, fires and human impact on the natural environment. A possible perspective would be to apply a combined methodology of soil development and charcoal dating to other sites in the Alps to investigate possible vegetation changes and treeline shifting.
Other sites would be of great interest for this kind of analysis, such as the Mediterranean area. The Mediterranean basin is affected by several fires almost every year, mostly due to the dry climatic conditions in the summer or due to man-made fires. The Mediterranean area has been one of the “glacial refuge” for many plant species during the ice age. The vegetation has undergone many changes throughout the centuries. Humans have established settlements in the Mediterranean region since their first appearance in the area and have continuously modified the natural environment. A reconstruction of the fire history in this region could be connected to the climate changes and show how (or if) the fire regimes have increased in the last centuries and if any changes in the vegetation have occurred. This study could also clarify the effects of fire on soil development, especially from a mineralogical point of view.

Application of other dating techniques (numerical and relative) which have not been used in the present work to the same site or to other Alpine sites:

- Dendrochronology: influence of changing climate on the tree development. Establishment of the forests and vegetation successions.
- Meteoric ^{10}Be in soils: relationship to soil evolution, ^{14}C dating and soil chemical and physical characteristics.
- Schmidt-hammer technique: relationship between the rebound values of the rocks near a boulder and the ^{10}Be age obtained by Surface Exposure Dating (SED).
- Weathering rinds: the degree of rock oxidation that can be related to the age of the surfaces (soil or boulders).

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Part B
Manuscripts

Manuscript I

Comparison of different methods of obtaining a resilient organic matter fraction in Alpine soils

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ABSTRACT

Soil organic matter (SOM) may give precious information about the age of soil landscapes and, thus, can contribute to decipher geomorphic surface dynamics. We tested five methods of isolating the oldest possible stable organic matter of 2 soil profiles developed on a Pleistocene morainic paragneiss substratum in an Alpine environment in northern Italy. Before and after the individual treatments, the organic fraction was dated with ^{14}C. The first two methods consist of the oxidation of organic matter with 10% hypochlorite (NaOCl), followed by dissolution of minerals with 10% hydrofluoric acid (HF) or 1 M aqua regia. Methods 3 and 4 were similar to the first two but with a changed order of the treatments (chemical oxidation as the last step). Method 5 consisted only of a treatment with hydrogen peroxide (H_2O_2) for 7 days. Methods 1–4 enabled, in theory, the separation of labile, mineral-protected and recalcitrant SOM fractions. With method 5 only two different fractions can be discerned, i.e. a labile one and a stable one. The lowest ages for each soil were obtained with methods 1–3 (5176 and 8835 cal BP). Higher ages were obtained with method 4 (aqua regia and NaOCl). In general, methods 1–4 showed increasing ages with increasing soil depth. The H_2O_2 treatment, however, left behind an organic fraction with the highest ages of up to 17,000 cal BP in the topsoil and decreasing ages with soil depth. In general, the ^{14}C ages of the treatment-resistant fraction increased in the order: untreated samples<method 3 (HF+NaOCl)≤method 1 (NaOCl+HF)≈method 2 (NaOCl+aqua regia)<method 4 (aqua regia+NaOCl)<method 5 (H_2O_2). Before and after the individual treatments, the fractions were analysed for their C and N content, functional groups were measured with FT-IR and complementary information was obtained with SEM-EDS. The changes in functional groups before and after the treatment with methods 1 and 3 were not very distinct. NaOCl was a too weak reagent to oxidise all labile organic matter in soils. It seems to work more or less properly only in soils with a low OC content. The use of HF produced artefacts such as the precipitation of cryolite. This could also influence organic matter (co-precipitation) and finally its age. HF treatment destroyed kaolinite and attacked quartz but did not have a great deal of effect on other phyllosilicates like mica. The subdivision of OM into a labile, mineral-protected and recalcitrant fraction using NaOCl and HF was consequently far from being precise. Consequently, these methods might be considered questionable. About 90% of organic C was oxidised with H_2O_2 (method 5) but only 60% of N removed. The remaining organic matter was enriched in nitrogen with a C/N ratio between 3 and 10, aliphatic, aromatic and amide compounds. H_2O_2 isolated the oldest and most stable OM pool. Our results indicate that the isolated organic matter after the H_2O_2 treatment can probably be used to estimate the age of the earliest formation of Holocene/Pleistocene-aged Alpine soils. The obtained ages corresponded well with the maximum age of charcoal fragments and the geomorphologic settings — in particular the end of the Egesen-equivalent glacial state and the oldest Dryas.

1. Introduction

Easily recognisable traces of dramatic climatic variations make high mountain areas unique geotopes and "storytellers" about past as well as potential future climate change effects on landscape dynamics and living conditions in regions of rugged topography. The general pattern of the glacial deposits in Alpine valleys can be associated with distinct readvance phases of the retreating ice-stream systems after the LGM (Last Glacial Maximum; 25,000–20,000 cal BP). However, the chronology of these lateglacial fluctuations is still poorly established and is based only on a few, often questionable minimum dates (e.g. basal samples of peat bogs), selected pollen profiles and the analysis of lake sediments. ^{14}C dates with varve counting indicated that alpine

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valleys (e.g. Upper Engadine, Switzerland) became ice-free prior to approximately 13,500 ^{14}C yBP (Ohlendorf, 1998). Most of the stadials older than Egesen (Younger Dryas; 11,000–10,000 ^{14}C yBP), i.e. equivalents of the Daun, Clavadel and Gschnitz stadials, still need direct links to an absolute time scale (e.g., Schlüchter, 1988; Kerschner, 2000; Ivy-Ochs et al., 2004).

Several methods exist that use soils to distinguish surfaces of different ages. However, many of these methods are far from being all suitable for use in the Alps (Fitze, 1982; Veit, 2002) and they give, furthermore, rather relative instead of absolute ages. Soil pH, translocation of organic matter, and development of typical spodic horizons all seem to attain a steady state within a few hundred to thousands of years (Egli et al., 2001). The dating of soil organic matter with ^{14}C could give a numerical value, if humified and stable substances that were produced almost at the beginning of soil formation were found and dated.

Soil organic carbon is known to contain a stable fraction with an old radiocarbon age, even though the stabilisation processes leading to the formation of this old soil carbon pool are not entirely clear (e.g. Eusterhues et al., 2003; Helfrich et al., 2007). Part of the organic carbon in soils is easily mineralised, whereas another carbon pool is known to degrade slowly at timescales from hundred to thousands of years (Oades, 1995). Since the conventional soil organic matter (SOM) fractionation in humic acids, fulvic acids and humin produce SOM pools that hardly differ with respect to turnover rates (Gamper, 1985; Balesdent, 1996) and contents of functional groups (Krosshavn et al., 1992), physical fractionation methods such as particle size and density fractionation have been proposed to analyse the processes of organic matter stabilisation in soils (Christensen, 1992; Golchin et al., 1997). Although the concept of OM fractionation into humic and fulvic acids and humins can be widely applied, the technique is operational and does not necessarily separate different types of molecules with a characteristic age (Hayes et al., 1989; Sutton and Sposito, 2005).

Three key processes have been proposed to explain the formation of passive or long residence time SOM fractions: (i) specific protection due to chemical recalcitrance, i.e. stabilisation due to the structural properties of the organic matter such as condensed and lignin-derived aromatic carbons, melanoidins, some tannins or aliphatic compounds (Anderson and Paul, 1984; Sollins et al., 1996; Baldock and Skjemstad, 2000; Krull et al., 2003; Poirer et al., 2003), (ii) spatial inaccessibility: inclusion of organic matter into aggregates or micropores, leading to physical protection of organic matter from microbial attack and (iii) sorption processes on minerals and interaction with metal ions that are known to play an important role in SOM preservation (Wiseman and Püttmann, 2006) and consequently influence the mean residence time of SOM (Saggar et al., 1996). Metal oxides have been demonstrated to be particularly effective in adsorbing and stabilising organic matter in soils (Kaiser and Zech, 1999; Wiseman and Püttmann, 2006). Nevertheless, the contribution and relative importance of these stabilisation mechanisms are not completely understood. Several authors have used different chemical treatments to extract the most stable OM (organic matter), followed by ^{14}C dating and in some cases also by comparing the ages of SOM with those of naturally-occurring charcoal fragments found in the same soils (Pessenda et al., 2001; Kleber et al., 2005; Eusterhues et al., 2005; Mikutta et al., 2006). Sodium hypochlorite (NaOCl) has been used to isolate a resistant OM fraction that is bond to mineral surfaces (Kaiser and Guggenberger, 2003). Acid hydrolysis is one of the procedures most commonly used to isolate stable OM because it preferentially removes young, potentially biodegradable compounds (e.g. proteins, nucleic acids and polysaccharides) and leaves behind an old C fraction (Paul et al., 1997, 2001). Acid hydrolysis is, however, inappropriate to distinguish between individual factors of OM stabilisation (e.g. Balesdent, 1996). Mikutta et al. (2006) performed the oxidation (first step) with NaOCl and used HF to liberate mineral-protected OM by dissolution of the mineral phase. The chemically resistant organic matter showed in most cases the oldest ^{14}C age. The formation of carbon pools with a long residence time was studied by Eusterhues et al. (2005) using H_2O_2. This treatment allowed the isolation of an organic matter fraction having an age of up to 6000 years that represents an actively stabilised fraction of soil organic matter.

A better understanding of ^{14}C age profiles in soils is, furthermore, rendered possible by the analysis of SOM fractions in the horizons and comparing them to fossil charcoal naturally buried at similar depths (Pessenda et al., 2001) or in the close neighbourhood of the studied site. Charcoal fragments found in the soils are often considered biologically inert and physically stable in relation to isotopic changes in the environment. Charcoal pieces are carbonised fragments of wood. They can give an indication about past fire frequency and paleobotanical proxies to reconstruct past vegetation composition and structure (Berli et al., 1994; Carcaillet and Thinon, 1996; Figueral and Mosbrugger, 2000; Ali et al., 2005;) and, since charcoal fragments >0.4 mm are usually not mass-transported by air more than a few metres from the source of ignition, they can be used to get additional information about landscape dynamics and soil evolution during the last thousands of years BP. In Alpine environments, charcoal fragments cannot be time-stratified, because of the possible soil bioturbation by soil fauna, soil reworking by uprooted trees and freeze–thaw processes (Carcaillet, 2001). The identification and dating of charcoal has given, however, additional information about soil evolution, landscape history and SOM storage (Figueral and Mosbrugger, 2000).

A comparison of this type of methodologies on the same soil profiles has rarely been done and consequently only a little data about comparable ^{14}C ages is available. Our aim was to determine the oldest possible SOM fraction in soils to obtain information about the minimum age of soil formation. We compared the techniques according to Mikutta et al. (2006) in which NaOCl and HF were used and the one according to Eusterhues et al. (2005) and Plante et al. (2004) in which H_2O_2 was used. In a third conceptual approach, we hypothesised that a changed order of NaOCl and HF application isolates more organic C that would be oxidised in a second step. We assumed that more aggregates would be destroyed using HF as a first step and, consequently, more mineral-protected OM would be liberated. This procedure should then leave behind an older organic C fraction. To reduce risks in handling samples, in an additional experiment we substituted HF by aqua regia (3 volumes of HCl 32%+1 volume of HNO_3 65%).

2. Materials and methods

2.1. Study area and investigation sites

The investigation area is located in Val di Rabbi, Trentino, in the south Alpine belt in northern Italy (Fig. 1). The climate of the valley ranges from temperate to alpine (above the timberline). Mean annual temperature varies from 8.2 °C in the valley floor to around 0 °C at 2400 m a.s.l., and mean annual precipitation approximately from 800 to 1300 mm/year (Servizio Idrografico, 1959). The timberline is close to 2000–2200 m a.s.l. and the forests are dominated by the conifers *Larix decidua* and *Picea abies* (Pedrotti et al., 1974). Above the timberline, alpine meadow is the typical vegetation type. The two investigated sites (Table 1; Fig. 1) were at 2100 m a.s.l. and at 2083 m a.s.l., and thus close to the timberline. The whole landscape near the investigation sites was strongly influenced by glaciers and both profiles developed on moraines (paragneiss). The investigated sites were covered by ice during the last glaciation period. According to the geomorphologic studies of Baroni and Carton (1990) or Filippi et al. (2007), surface ages can be estimated to be around 14,000 to 16,000 years.

The soil profiles were selected during a soil cartographic inventory and can be considered as undisturbed and representative of the

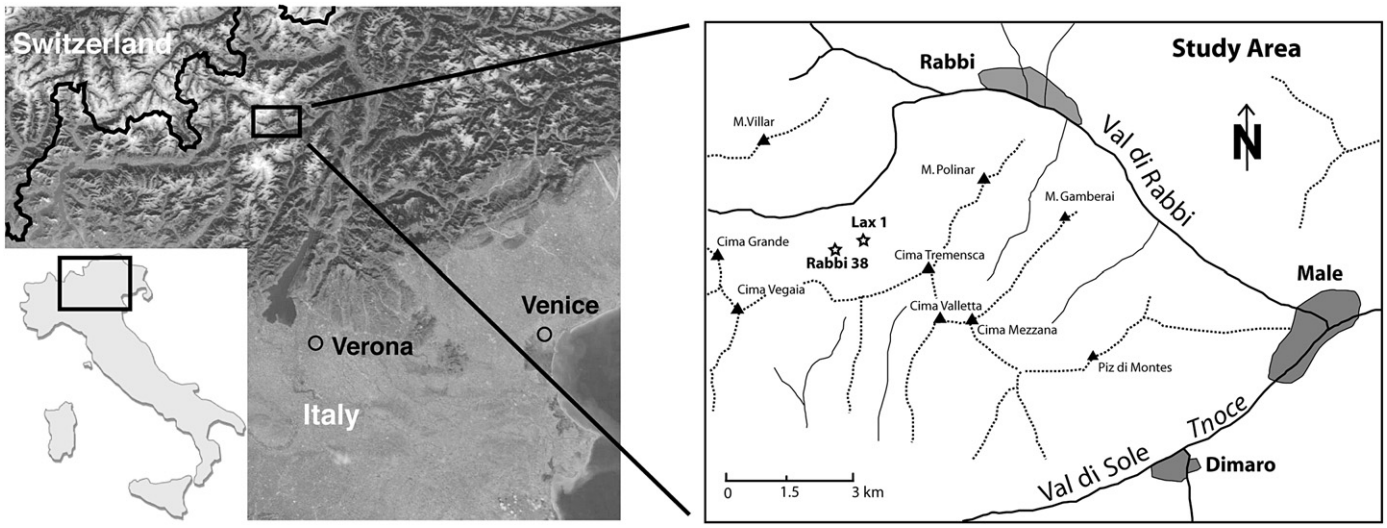

Fig. 1. Location of the investigated sites.

elevation zones. Both soils can be classified as *Entic Podzols* (*Skeletic*) according to the WRB (IUSS Working Group, 2006). According to Soil Taxonomy (Soil Survey Staff, 2006), the soil moisture regime is udic (humid conditions, <90 days/year with a dry soil) at all sites and the soil temperature regime is cryic (mean annual temperature <8 °C, no permafrost). Maximum precipitation occurs during the summer months. Special attention was given to ensure that the soils showed an undisturbed evolution with almost no signs of erosion or burial. Soil material was collected from excavated pits and samples of undisturbed soil were taken, where possible, down to the BC horizon. Around 2 to 4 kg of soil material (Hitz et al., 2002) were collected per soil horizon.

2.2. Soil chemistry and physics

The samples were air-dried, large aggregates were gently broken by hand and sieved to <2 mm. Total C and N contents of the soil were measured with a C/H/N analyser (Elementar Vario EL, elementar Analysensysteme GmbH) using oven-dried and ball-milled fine earth. In this case total C corresponds to organic C due to the absence of any carbonates in the soil. Soil pH (in 0.01 M $CaCl_2$) was determined on air-dried samples of fine earth using a soil solution ratio of 1:2.5. After a pre-treatment of the samples with H_2O_2 (3%), particle size distribution of the soils was measured using a combined method consisting of sieving the coarser particles (2000–32 μm) and the measurement of the finer particles (<32 μm) by means of an X-ray sedimentometer (SediGraph 5100). The dithionite- (Fe_d, Al_d) and oxalate-extractable (Fe_o, Al_o) fractions were measured according to McKeague et al. (1971). The elemental concentrations were determined by atomic absorption spectroscopy.

Table 1
Characteristics of the study sites

Profile	Elevation (m a.s.l.)	Aspect	Slope	Parent material	Vegetation	Land use	WRB (IUSS Working Group, 2006)
Rabbi 38	2100	60°N	32%	*Paragneiss*	*Larix decidua* *Juniperus* spp.	Natural Forest	*Entic Podzol* (*Skeletic*)
Lax 1	2083	240°N	32%	*Paragneiss*	*Larix decidua* *Juniperus* spp.	Natural Forest	*Entic Podzol* (*Skeletic*)

Functional groups and compounds of organic matter as well as some mineralogical features were determined by FT-IR measurement (Bruker, Tensor 27). Spectra were recorded from 4000 to 250 cm^{-1} on pellets made with 1 mg of sample and 250 mg of KBr heated at 150 °C. Major IR absorption bands and functional groups assignments are given in Table 2. Relative peak intensities were used for quantitative analysis using the software OPUS 6.

2.3. Charcoal

Both soil profiles were sampled for charcoal. Large charcoal fragments were found only in one of them. The identification and dating of charcoal gives a rough idea about fire events, plant communities and landscape evolution. Charcoal was separated from the soil material and dried at 40 °C. Being fragile, the charcoal was handled very carefully to reduce any mechanical stress as much as possible. To identify the sources of charcoal, the individual particles were analysed microscopically. The charcoal was investigated in the dry state; micro sections were cut by hand with a razor blade to show the transverse section. Charcoal classification was restricted to black, completely opaque, angular fragments, a conservative criterion necessary to ensure origin by fire (Clark, 1988). The charcoal fragments were separated into coniferous and broad-leaved tree species (Schoch,

Table 2
Major IR absorption bands and assignments (Piccolo and Mirabella, 1985; Stevenson, 1994; Senesi et al., 2003; Tan, 2003)

Band	Wave number cm^{-1}	Assignment
1	2976–2937	Aliphatic C–H stretching (aliphatic methyl and methylene groups)
2	1725–1710	C═O stretching of COOH, aldehydes and ketones
3	1660–1630	C═O stretching of amide groups, quinone C═O and/or C═O of H-bonded conjugated ketones
	1620–1600	Aromatic C═C, strongly H-bonded C═O of conjugated ketones
4	1535–1510	Aromatic rings, amide II vibrations
5	1460–1440	Aliphatic C–H stretching
6	1413–1333	OH deformation and C–O stretching of phenolic groups
7	1280–1200	C–O stretching and OH deformation of COOH, C–O stretching of aryl ethers and phenols
8	1180–1050	C–O stretching of polysaccharide

1986) using a stereomicroscope (magnification 6.4–40×, Wild M3Z Leica, Germany). The charcoal fragments from the coniferous trees were divided further at the genus level using a reflected-light microscope (objective 5×, 10×, and 20×, Olympus BX 51, Japan). The observations were compared with a histological wood-anatomical atlas, using an identification key (Schweingruber, 1990). Charcoal samples were treated with hydrochloric acid, followed by a treatment with sodium hydroxide to remove humic acids formed during the rotting process.

2.4. Radiocarbon dating

The samples (soil or charcoal fragments) were heated and catalytically reduced over cobalt powder at 550 °C to elemental carbon (graphite). This mixture was pressed into a target and the ratios ^{14}C:^{12}C were measured by Accelerator Mass Spectrometry (AMS) using the tandem accelerator of the Institute for Particle Physics at the Swiss Federal Institute of Technology Zürich (ETH). The calendar age was obtained using the CalibETH calibration program (Niklaus, 1991).

2.5. Fractionation of organic matter

Our conceptual approach was based on the finding that partial oxidative degradation of OM leaves behind intrinsically resistant as well as mineral-protected organic materials. We treated the soils using five different methodologies (Table 3) to eliminate more labile organic material from more refractory organic matter having a longer mean residence time (Eusterhues et al., 2005; Mikutta et al., 2006; Plante et al., 2004).

i) The first two methods were based on the oxidation of "fresh" OM by 10% NaOCl followed by mineral dissolution using 10% HF (method 1; Mikutta et al., 2006, modified) or 1 M aqua regia (method 2). Eight grams of air-dried soil samples were treated with 80 ml of 10 wt.% NaOCl, which was adjusted to pH 8.0 by adding 32% HCl. Three treatment cycles of 6 h were performed at 25±1 °C. Samples were then centrifuged (2574 ×*g*; 5 min), decanted, and the residues washed three times with 60 ml 1M NaCl by hand stirring, then centrifuged and the supernatant discarded. The residues were then washed from NaCl with deionised water to reach an electrical conductivity of <40 µs cm^{-1} and freeze-dried. The NaOCl-treated samples were subsequently extracted with 10% HF or 1 M aqua regia in order to dissolve minerals and release stabilised OM. After the NaOCl treatment, weights were recorded, C and N analyses done and ^{14}C dating performed. In the subsequent step, 3 g of freeze-dried samples were transferred into pre-weighted plastic bottles and treated four times with 20 ml 10% HF or 20 ml 1 M aqua regia (experiment in parallel on the same sample). The samples were shaken for 2 h at 150 rpm, centrifuged (2574 ×*g*; 5 min), and the supernatant discarded. The residues were washed five times with 20 ml deionised water and freeze-dried. The same types of analyses as performed after the NaOCl treatment were done on both residues.

Table 3
Overview of the methodologies used for stable organic matter extraction

	Method 1	Method 2	Method 3	Method 4	Method 5
Step 1	10% NaOCl	10% NaOCl	10% HF	1 M Aqua Regia ($HCl+HNO_3$)	10% H_2O_2
Step 2	10% HF	1M Aqua Regia ($HCl+HNO_3$)	10% NaOCl	10% NaOCl	–

After the HF or aqua regia treatment, the amount of organic C was related to the initial content with a mass-balance approach to obtain the corresponding recoveries with

$$(gC_{after}/gC_{before}) \times 100 \quad (1)$$

The same recoveries were calculated for the amounts of N and of dry matter.

ii) The approach for methods 3 and 4 is similar to that of methods 1 and 2 but with a changed order of treatments, i.e. chemical oxidation as the last step. Briefly, 7.5 g of untreated soil were treated four times with 50 ml of 10% HF (= method 3) or with 1 M aqua regia (= method 4). The samples were shaken for 2 h at 150 rpm, centrifuged (2574 ×*g*; 5 min), and the supernatant discarded. The residues after the HF treatment were transferred into centrifuge tubes and washed with 50 ml deionised water five times. The samples were then freeze-dried and the weight recorded. Parts of the HF and aqua regia residues were used for ^{14}C dating and total C and N measurement. Four grams of the freeze-dried residues were transferred into 250 ml plastic bottles to perform the oxidation. Using 40 ml of 10% NaOCl, the samples were shaken after three treatments (cycles of 6 h), centrifuged (2574 ×*g*; 5 min) and the supernatant discarded. The residues were then washed 3 times by stirring in centrifuge tubes using 30 ml of 1 M NaCl. Subsequently, the removal of NaCl was performed using 30 ml of deionised water until the electrical conductivity was <40 µs cm^{-1}. The samples were then freeze-dried and the weight recorded, ^{14}C dated and analysed for C and N.

iii) The third conceptually different technique (= method 5) is based on the oxidation of the OM by 10% H_2O_2 (Plante et al., 2004; Eusterhues et al., 2005, modified). 1 g of air-dried soil was wetted for 10 min using distilled water in a 150-ml beaker. Afterwards, 90 ml of 10% H_2O_2 were added. The procedure was run at a minimum temperature of 50 °C throughout the treatment period. The beakers were closed with two layers of parafilm to avoid evaporation of the reagent. Peroxide treatments were performed for 168 h (7 days). At the end of the treatment the samples were washed three times with 40 ml deionised water and freeze-dried, the weight recorded, analysed for total C and N and ^{14}C dated.

2.6. SEM and EDS analyses

Selected treated and untreated soil samples were analysed by scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). The samples were prepared for the SEM analysis by first sonicating 10 µg of material for 30 s in 10 ml of deionised water and then transferring 60 µl of the solution onto standard aluminium Al-SEM stubs covered with aluminium foil. The analysis was performed using a Philips XL20 SEM operating at an accelerating voltage of 20 kV. Identification of minerals and organic matter was aided by the use of EDS which provided an elemental composition of the solid phases analysed. The EDS detector was equipped with an ultra-thin window allowing detection of elements down to carbon.

2.7. Isotopic analysis of organic matter fractions

Following archaeological protocol, conventional radiocarbon ages were calculated using the Libby half-life (5568 years; mean life 8033 years) rather than the correct value of 5730 years (Stuiver and Polach, 1977) and were referenced to 1950. Conventional radiocarbon age provides a qualitative indication of C residence time and stability (Mikutta et al., 2006). The isotopic content (*I*) of labile OC pools could not be measured directly. The *pMC* (percent of modern carbon) of

NaOCl (H_2O_2)-removable OC (LOC), HF (aqua regia)-removable OC (MOC) were calculated from mixing models (Mikutta et al., 2006):

$$I - C_L = \frac{((I - C_U) \cdot UOC - (I - C_S) \cdot SOC)}{LOC} \quad (2)$$

$$I - C_M = \frac{((I - C_S) \cdot SOC - (I - C_R) \cdot ROC)}{MOC} \quad (3)$$

where $I-C_U$, $I-C_L$, $I-$– C_S, $I-C_M$ and $I-C_R$ are, respectively, the values of untreated, NaOCl removable, NaOCl resistant (stable), mineral-protected and chemically resistant OM. UOC (*untreated OC*), LOC (*labile OC*), SOC (*stable OC*), MOC (*mineral-protected OC*) and ROC (*resistant OC*) correspond to the respective OC contents.

3. Results

3.1. Soil characteristics

The soils are acidic and have a high SOM content in the surface horizon. They are furthermore characterised by a high proportion of soil skeleton that is typical for Alpine soils on a morainic substratum. The soils exhibited a sandy loam to loamy texture; the proportion of sand decreased towards the soil surface, and silt and clay correspondingly increased (Table 4). The upward decrease of the grain sizes is a concomitant effect of weathering. The soils are well developed and have a bleached horizon followed by a horizon with an accumulation of sesquioxides. Consequently, the soils show an eluviation and illuviation of Fe and Al (Table 4).

3.2. Fractionation of organic matter

3.2.1. Qualitative aspects of organic matter fractions

Depending on the soil and horizon, the NaOCl treatment decreased the OC content by about 36–62% of the initial OC and ranged between 8.4 and 71.6 g kg^{-1} soil (Table 5). NaOCl resistant N was with 0.3–2.2 g kg^{-1} very low and represented around 25–50% of the initial content. HF treatment released 25% of the NaOCl resistant organic carbon which corresponds to the mineral-protected organic carbon (MOC) and around 14% of N. Aqua regia treatment, after NaOCl, reduced the sample weight less than with HF, but released 26% of the stable OC and 12% of the NaOCl-stable N (both values almost identical to the HF treatment) (Table 5). After the HF treatment (method 3), a distinct increase in the OC and N concentration was measured in both profiles in the upper horizons (Table 5). These results are consistent with findings of Schmidt and Gleixner (2005). HF reacts with silicates and oxides to form soluble fluoride complexes, but is expected to leave organic matter mostly unaffected (Eusterhues et al., 2007). It is used to enrich soils and sediments in organic matter before pyrolysis (Zegouagh et al., 2004). In the second step of the treatment, hypochlorite oxidised a part of the OM and generally decreased the OM concentration.

HF as the first step reduced the dry matter by about 50% in both profiles and hypochlorite as the second step by about 10%. The aqua regia treatment led to a decrease in OC of about 65–70% and 17–30% for N. The NaOCl treatment after aqua regia additionally decreased the C content to about 7 and 15% and the N content to 40 and 55% in the 1st and 2nd profiles respectively (Table 5). The differences between the procedures using HF or aqua regia were distinct with respect of the OC and N content as well as the C/N ratio (Table 5). The concentrations of OC and N after the different steps were much lower with the aqua regia procedure. Aqua regia did not dissolve that much silicate minerals. In addition, the C/N ratios were different, especially in the subsoil, having lower values when using the aqua regia procedure. In the subsoil, N-rich organic compounds that are strongly associated with (clay) minerals are less attacked by aqua regia and by the subsequent oxidation with NaOCl. In contrast, HF seems to dissolve such relatively stable mineral-organic matter complexes due to a partial dissolution of phyllosilicates.

The hydrogen peroxide (H_2O_2) method was the most effective in reducing the C content. Profile 1 had a carbon concentration ranging from 2.1 to 15 g/kg after the treatment. This corresponds to an oxidised percentage of about 90% (Table 5). The highest resistance to oxidation with 15 g/kg soil or 25% of the initial total organic carbon was found in the BE horizon. In both profiles, the decrease in total N was less expressed compared to that of C, and thus gave rise to low C/N ratios. This finding is in agreement with Schulten et al. (1996) and Cheshire et al. (2000) who found oxidation-resistant organic matter enriched in N-compounds.

3.2.2. Recovery of dry matter

The recovery of mass after methods 1 and 3 (using HF) was always around 30–40% (Table 6). More mass, usually between 62 and 74%, was recovered using aqua regia (methods 2 and 4) instead of HF. The difference is mainly due to the dissolution of silicatic bonds (Si–O) with HF (Rumpel et al., 2006). Mass recovery with H_2O_2 was in a similar range as those obtained by the other methods using aqua regia.

3.2.3. Recovery of org. C

Methods 1 and 2 (hypochlorite followed by HF or aqua regia): about 50% of the initial C mass was oxidised after the NaOCl treatment. Additional organic C was removed after the application of HF or aqua regia, so that at the end about 7–18% of the initial amount of C remained. In profile Rabbi 38, the recovery generally decreased with soil depth while in the other profile no trend with depth could be observed. In most cases, the procedure with aqua regia gave similar results to HF, except for the AE horizon of Lax 1.

Table 4
Selected properties of the investigated soils

Profile/horizon	Soil depth(cm)	Colour	Skeleton[a] (%)	pH ($CaCl_2$)	C_{tot} (g kg^{-1})	N (g kg^{-1})	Sand[b] (g kg^{-1})	Silt (g kg^{-1})	Clay (g kg^{-1})	Al_d (g/kg)	Fe_d (g/kg)	Al_o (g/kg)	Fe_o (g/kg)
Rabbi 38													
AE	2–4	10YR 3/3	4.6	3.70	102.5	5.7	455	280	265	2.51	15.94	1.73	5.57
BE	4–8	5YR 4/4	34.1	3.60	60.3	2.9	515	280	205	2.88	20.56	1.91	6.06
Bs1	8–20	7.5YR 4/4	10.0	4.10	38.9	1.8	575	286	139	14.71	44.13	10.27	19.62
Bs2	20–45	10YR 4/4	51.1	4.40	16.8	0.7	671	275	54	7.34	21.49	5.84	9.37
Lax 1													
AE	5–11	10YR 4/3	6.8	3.50	56.2	2.7	437	302	261	3.16	21.11	2.18	7.13
Bs1	11–26	5YR 4/6	15.8	3.85	34.9	1.7	551	344	105	9.55	50.72	6.42	20.19
Bs2	26–50	7.5YR 4/6	47.1	4.25	22.5	1.1	663	258	79	8.65	24.56	6.35	10.08

[a] Skeleton = material > 2 mm in diameter.
[b] Size fractions: sand = 2000 – 62 μm, silt = 62 – 2 μm, clay = < 2 μm.

Table 5
Total organic C (OC), nitrogen (N) and C/N ratios of SOM before and after every single treatment

Untreated samples			
Profile/horizon	OC (g kg^{-1})	N (g kg^{-1})	C/N
Rabbi 38			
AE	102.5	5.7	18
BE	60.3	2.9	21
Bs1	38.9	1.8	22
Bs2	16.8	0.7	24
Mean	54.6	2.8	21
Lax 1			
AE	56.2	2.7	21
Bs1	34.9	1.7	21
Bs2	22.5	1.1	20
Mean	42.1	2.1	21

	Method 1						Method 2		
	1st step	NaOCl		2nd step	HF		2nd step	AqR[a]	
Profile/horizon	OC (g kg^{-1})	N (g kg^{-1})	C/N	OC (g kg^{-1})	N (g kg^{-1})	C/N	OC (g kg^{-1})	N (g kg^{-1})	C/N
Rabbi 38									
AE	71.6	2.2	32	49.5	1.1	46	30.7	0.7	42
BE	28.1	0.7	41	24.0	0.4	67	14.2	0.4	40
Bs1	10.1	0.3	37	9.9	0.5	21	2.6	0.3	10
Bs2	8.4	0.3	25	3.1	0.3	10	2.4	0.2	12
Mean	29.6	0.9	34	21.6	0.5	36	12.5	0.4	26
Lax 1									
AE	29.9	1.5	20	16.5	0.7	24	22.3	0.9	25
Bs1	24.0	1.4	17	22.2	1.4	16	5.9	0.6	9
Bs2	20.5	1.0	20	6.7	0.6	12	3.0	0.6	5
Mean	26.0	1.2	23	16.8	0.8	22	10.9	0.6	16

	Method 3						Method 4					
	1st step	HF		2nd step	NaOCl		1st step	AqR[a]		2nd step	NaOCl	
Profile/horizon	OC (g kg^{-1})	N (g kg^{-1})	C/N	OC (g kg^{-1})	N (g kg^{-1})	C/N	OC (g kg^{-1})	N (g kg^{-1})	C/N	OC (g kg^{-1})	N (g kg^{-1})	C/N
Rabbi 38												
AE	192.1	9.8	20	210.3	9.5	22	69.6	4.2	16	47.4	1.8	26
BE	128.4	6.2	21	104.9	4.1	26	17.9	1.0	17	30.5	0.9	33
Bs1	38.6	2.4	16	19.4	0.9	22	7.8	0.9	8	4.9	0.5	9
Bs2	9.7	0.7	15	4.0	0.3	15	5.2	0.5	11	2.1	0.4	5
Mean	92.2	4.8	18	84.7	3.7	21	25.1	1.7	13	21.2	0.9	18
Lax 1												
AE	114.1	4.4	26	107.0	3.1	35	39.0	2.1	18	25.3	1.0	26
Bs1	67.8	3.6	19	22.5	0.8	29	12.7	1.3	10	6.2	0.6	11
Bs2	15.6	1.0	16	5.1	0.3	17	5.0	0.7	7	3.6	0.5	7
Mean	72.4	3.4	20	54.8	2.0	26	20.4	1.4	12	14.1	0.8	15

	Method 5				
	Untreated			1st step	H_2O_2
Profile/Horizon	OC (g kg^{-1})	N (g kg^{-1})	C/N	OC (g kg^{-1})	N (g kg^{-1})	C/N
Rabbi 38						
AE	102.5	5.7	18	8.6	1.2	7
BE	60.3	2.9	21	15.0	1.2	13
Bs1	38.9	1.8	22	4.1	1.3	3
Bs2	16.8	0.7	24	2.1	0.7	3
Mean	54.6	2.8	21	7.5	1.1	6
Lax 1						
AE	56.2	2.7	21	2.8	0.9	3
Bs1	34.9	1.7	21	6.5	1.3	5
Bs2	22.5	1.1	20	6.6	0.8	9
Mean	42.1	2.1	21	5.8	1.0	6

[a] AqR = aqua regia treatment.

Methods 3 and 4 (HF or aqua regia followed by hypochlorite): in contrast to our expectations, the changed order of reagents with HF or aqua regia as the first step led to a higher recovery of C. With HF and NaOCl, up to 77% of the original amount of C remained unaffected. Especially in the topsoil, the differences to method 1 were large while in the subsoil almost the same values were obtained.

Method 5 (H_2O_2): C recovery was very low after the hydrogen peroxide treatment. In contrast to the other two methods, the H_2O_2 treatment generally led to an increase of the recovery value with soil depth. Much more organic matter was oxidised in the topsoil than with the other two methods. In the subsoil, less organic matter was removed compared to the other methods.

3.2.4. Recovery of N

Methods 1 and 2: in the soil of Rabbi 38, a substantial amount of the initial N was already eliminated after the NaOCl treatment

Table 6
Recoveries (ratio of measured amount to the initial amount) of organic C, nitrogen and dry matter after each treatment and method

Organic C	No. of treatment	Method 1		Method 2		Method 3		Method 4		Method 5
		NaOCl	HF	NaOCl	AqR	HF	NaOCl	AqR	NaOCl	H_2O_2
Site/horizons	org. C	org. C	org. C	org. C	org. C	org. C	org. C	org. C	org. C	org. C
	%	%	%	%	%	%	%	%	%	%
Rabbi 38										
AE	100	50.6	17.5	50.6	18.8	101.3	70.3	56.0	32.3	5.9
BE	100	37.3	13.7	37.3	15.7	103.9	67.2	24.8	36.4	17.4
Bs1	100	21.2	9.6	21.2	4.2	47.6	20.3	14.4	8.3	5.3
Bs2	100	40.8	7.0	40.8	9.0	26.1	9.0	24.3	8.6	28.3
Lax 1										
AE	100	48.5	9.9	48.5	32.5	103.1	76.9	59.9	32.2	3.5
Bs1	100	58.5	18.4	58.5	10.5	85.7	22.3	27.1	11.9	14.9
Bs2	100	84.3	11.3	84.3	9.5	35.8	9.1	17.7	11.8	20.5
Nitrogen	No. of treatment	Method 1		Method 2		Method 3		Method 4		Method 5
		NaOCl	HF	NaOCl	AqR	HF	NaOCl	AqR	NaOCl	H_2O_2
Site/horizons	N	N	N	N	N	N	N	N	N	N
	%	%	%	%	%	%	%	%	%	%
Rabbi 38										
AE	100	28.5	6.8	28.5	8.2	92.8	57.2	61.0	22.5	14.7
BE	100	18.7	4.3	18.7	8.1	104.3	54.5	30.0	23.1	29.0
Bs1	100	12.4	9.8	12.4	9.0	65.0	19.6	37.4	19.2	36.1
Bs2	100	38.6	16.1	38.6	18.5	43.1	14.1	51.6	41.6	76.6
Lax 1										
AE	100	50.5	8.6	50.5	27.6	83.3	46.0	67.5	26.1	23.3
Bs1	100	70.5	23.4	70.5	23.8	92.4	15.9	57.6	22.1	61.2
Bs2	100	87.6	20.0	87.6	39.0	46.4	11.0	51.0	35.6	48.4
Dry matter	No. of treatment	Method 1		Method 2		Method 3		Method 4		Method 5
		NaOCl	HF	NaOCl	AqR	HF	NaOCl	AqR	NaOCl	H_2O_2
Site/horizons	mass	mass	mass	mass	mass	mass	mass	mass	mass	mass
	%	%	%	%	%	%	%	%	%	%
Rabbi 38										
AE	100	72.5	36.1	72.5	62.9	54.1	34.3	82.4	69.7	70.0
BE	100	80.0	34.4	80.0	66.6	48.8	38.6	83.7	72.1	70.0
Bs1	100	81.3	37.7	81.3	62.4	47.9	40.5	71.7	66.1	50.0
Bs2	100	81.3	37.7	81.3	64.4	45.0	38.1	78.6	69.4	80.0
Lax 1										
AE	100	91.3	33.8	91.3	82.2	50.8	40.4	86.3	71.5	70.0
Bs1	100	85.0	28.9	85.0	62.3	44.1	34.6	74.5	66.7	80.0
Bs2	100	92.5	38.0	92.5	70.9	51.5	40.2	80.6	73.5	70.0

AqR = aqua regia treatment.

while in the other soil a large part remained unaffected. The subsequent treatment with HF gave slightly lower recoveries than with aqua regia. In contrast to C, the recoveries increased with soil depth for both treatments — HF and aqua regia. The resistant organic matter in the subsoil was consequently richer in nitrogen.

Methods 3 and 4: The changed order of the reagents led to much higher recoveries. Especially with HF, the removal was – except for the subsoil – very ineffective. Compared to HF, aqua regia eliminated more N. In contrast to method 1, a decrease of recoveries was measured with soil depth using HF. Using aqua regia a slight increase can be

Table 7
Calibrated radiocarbon (^{14}C) ages of soil organic matter fractions and charcoal

Profile/horizon	Not treated		Method 1	Method 2	Method 3		Method 4		Method 5	Charcoal
	Samples	NaOCl (Step 1)	HF (Step 2)	AqR (Step 2)	HF (Step 1)	NaOCl (Step 2)	AqR (Step 1)	NaOCl (Step 2)	H_2O_2	
Rabbi 38										
AE	Modern	Modern	Modern	Modern	n.d.	n.d.	n.d.	n.d.	14,683±313	–
BE	Modern	228±75	438±69	616±42	Modern	Modern	357±65	606±40	17,729±237	–
Bs1	712±24	1825±57	3692±77	3854±72	n.d.	n.d.	n.d.	n.d.	11,626±213	–
Bs2	2929±55	4915±53	8835±116	8251±65	3342±58	8051±82	6385±56	10,946±142	11,068±147	–
Lax1										
AE	130±106	418±70	n.d.	609±41	130±106	369±64	502±32	589±43	10,851±174	3271±65
Bs1	590±44	985±50	1942±52	1803±60	n.d.	n.d.	1324±30	2843±50	9104±96	3278±67
Bs2	1432±63	2623±99	5176±101	5781±87	1912±61	5884±94	3962±83	7981±66	8498±64	10,353±86

n.d. = not determined.

measured, but the recoveries were distinctly higher than with method 1.

Method 5 (H_2O_2): low N recoveries were recorded for the topsoil. In the subsoil, however, only a minor part of N was oxidised and recoveries values were up to 60–70% (Tables 5 and 6).

3.3. Radiocarbon ages of SOM fractions

Methods 1 and 2: a distinct increase in age was measurable from untreated to NaOCl-treated (1st step) and to HF or aqua regia treated (2nd step) samples. Although the fractionation of organic carbon with HF and aqua regia was different, the obtained ages at the end of the treatment procedure were almost identical (Table 7). The obtained ages after the treatments ranged from "modern" to 8835 ± 116 cal BP in the first profile, and from 609 ± 41 to 5781 ± 87 cal BP in the second (Table 7).

Methods 3 and 4: the distribution of the different C fractions showed a greater recalcitrant pool, together with a distinct decrease in the C/N ratio, especially after the application of aqua regia. Although less carbon was removed compared to methods 1 and 2, the obtained ages were partially higher. They went up to 10946 ± 142 cal BP in the first profile, and up to 7981 ± 66 cal BP in the second one (Table 7; method 4). In both profiles, an increase in age with soil depth was measured, similar to methods 1 and 2. The changed order of reagents obviously destroys less total organic matter, but eliminates more young organic matter. The aqua regia can be used as a reagent that clearly leaves behind an old OM pool. Aqua regia is in this respect at least equally as powerful as HF in obtaining a stable organic fraction.

Method 5: the obtained ages of OM that resisted H_2O_2 were definitively the highest compared to the other methods. They varied from 11,068 ± 147 to 17,729 ± 237 cal BP in the first profile, and from 8498 ± 64 to 10,851 ± 174 cal BP in the second (Table 7). Additionally, the age trend within the soil profile was different to that obtained using the other methods (cf. also Eusterhues et al., 2003, 2005; Mikutta et al., 2006; Rumpel et al., 2006). Surprisingly, the highest ages were measured in the topsoil. This would, however, be logical when one takes into account that soil organic matter that derives from organic litter and dead roots is produced first in the topsoil and not in the subsoil. In contrast to the opinion of many authors (e.g. Scharpenseel and Becker-Heidmann, 1992; Rumpel et al., 2002), the oldest organic matter fraction can under certain circumstances still be found in the topsoil — if a suitable reagent is used that allows its detection.

3.4. Charcoal

Charcoal pieces were occasionally found in soils of the investigated area. Dating of charcoal fragments from the horizons of the second profile (Lax 1) gave increasing ^{14}C ages with soil depth varying from 3271 ± 65 cal BP in the upper horizon to 10,353 ± 86 cal BP in the lower one (Table 7). Because the oldest charcoals were found in the lower horizons, the increase of age with increasing soil depth can be explained by a downward migration of charcoal caused by soil fauna or soil water (Carcaillet, 2001). The charcoal fragments could be identified as *Larix* and *Pinus* — the same kind of trees that actually dominate the forest. After about 150–300 years of soil formation, Larix-trees are the first able to grow at such an altitude according to the plant succession model of Burga (1999). The measured age of 10,353 yBP of the charcoal and the minimum time necessary for tree growth would give a minimum age of soil formation of about 10,600 yBP which corresponds very well with the measured age of the resistant organic matter fraction in the surface horizon after the H_2O_2 extraction.

3.5. FT-IR and SEM analyses

FT-IR spectra of the H_2O_2-treated samples showed that the oxidation-resistant OM is relatively enriched in aliphatic, aromatic and amide compounds (Figs. 2 and 3) as found also by Theng et al. (1986) and Leifeld and Kögel-Knabner (2001). The other methods did not show a great relative difference before and after the treatment. The aromatic band shifts measured on the H_2O_2-resistant fraction are most probably due to the presence of charcoal-like substances. H_2O_2 was very effective in removing organic matter which was clearly visible with SEM (Fig. 4). However, charcoal particles remained. SOM in between soil minerals and consequently adsorbed on mineral surfaces partially remained. SEM analyses demonstrated that H_2O_2 did not attack minerals but almost completely destroyed the soil organic matter, leaving a few unaltered charcoal fragments (Fig. 4).

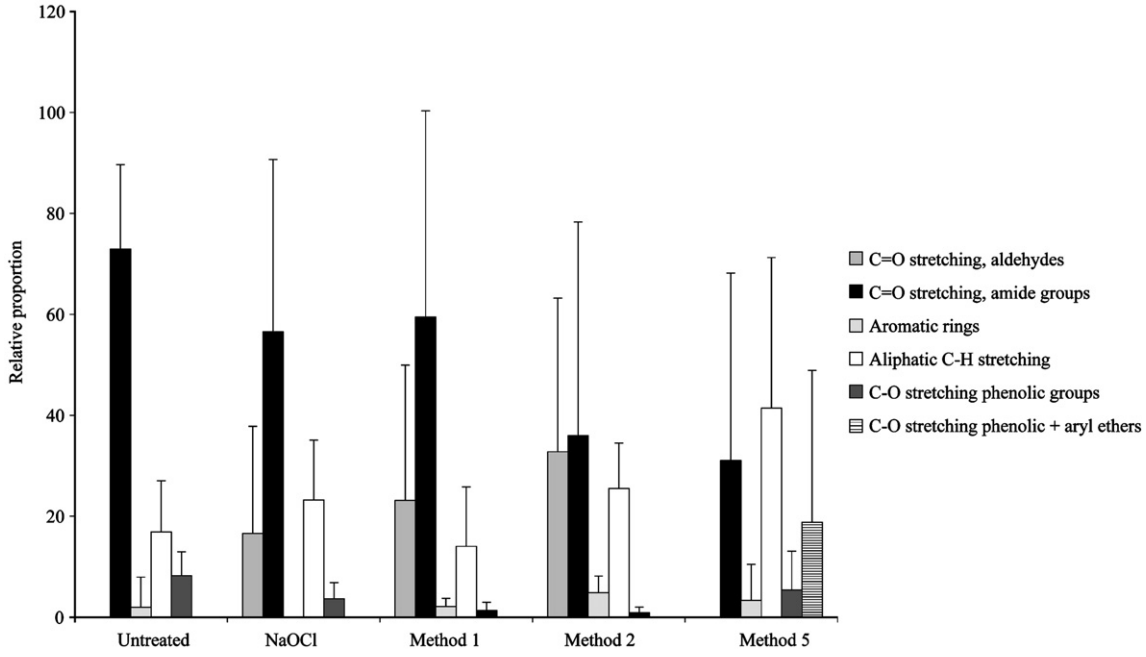

Fig. 2. Mean distribution (relative proportion) of the IR-bands (and corresponding functional groups) before (untreated) and after the different treatments.

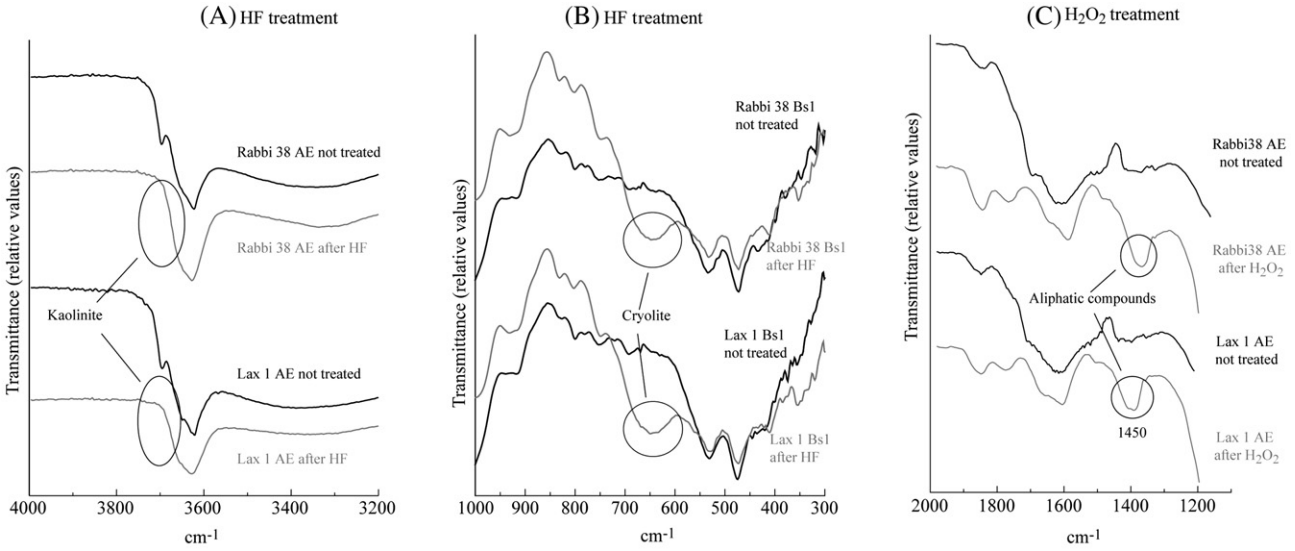

Fig. 3. Comparison of FT-IR spectra before any treatment and (A and B) after the HF treatment (method 1) and (C) after the H_2O_2 treatment (method 5).

NaOCl and HF (method 1) were not very effective in removing organic matter: larger, single organic tissues having most probably a low ^{14}C age, small roots, etc. remained (Fig. 4). Many organic particles also then remained in the soil sample when HF was first used followed by NaOCl (method 3). HF seemed particularly to attack quartz and dissolve phytoliths. Quartz grains had many and quite severe fissures whereas other minerals like mica seemed to be much less affected (Fig. 4). Quartz in the untreated sample showed no distinct fissures. This effect can, thus, be definitely attributed to the HF treatment. The untreated sample had, unsurprisingly, a higher amount of OM.

After HF treatment, FT-IR analyses showed the dissolution of silicate minerals and the formation of artefacts (cryolite, a sodium aluminium fluoride) (Fig. 3).

3.6. Correlation analyses

The untreated soil material showed a positive correlation between OC and clay content (Fig. 5). This is not necessarily a proof that SOM is stabilised and protected from decay by clay minerals because both parameters also are a function of soil depth. Except for the H_2O_2

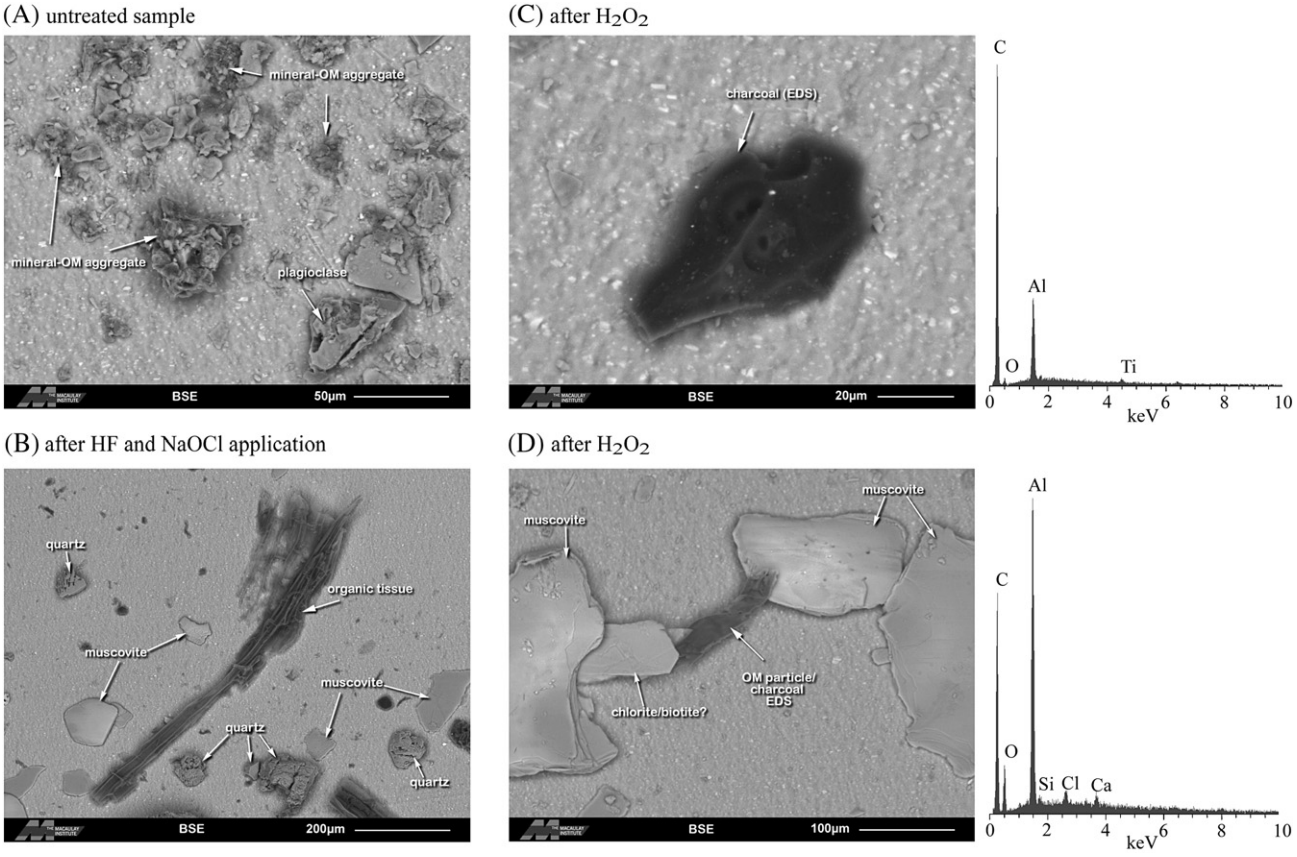

Fig. 4. SEM micrographs with EDS analyses of untreated (A), HF+NaOCl-treated (B) and H_2O_2-treated (C and D) samples of the Bs1 horizon (Rabbi 38).

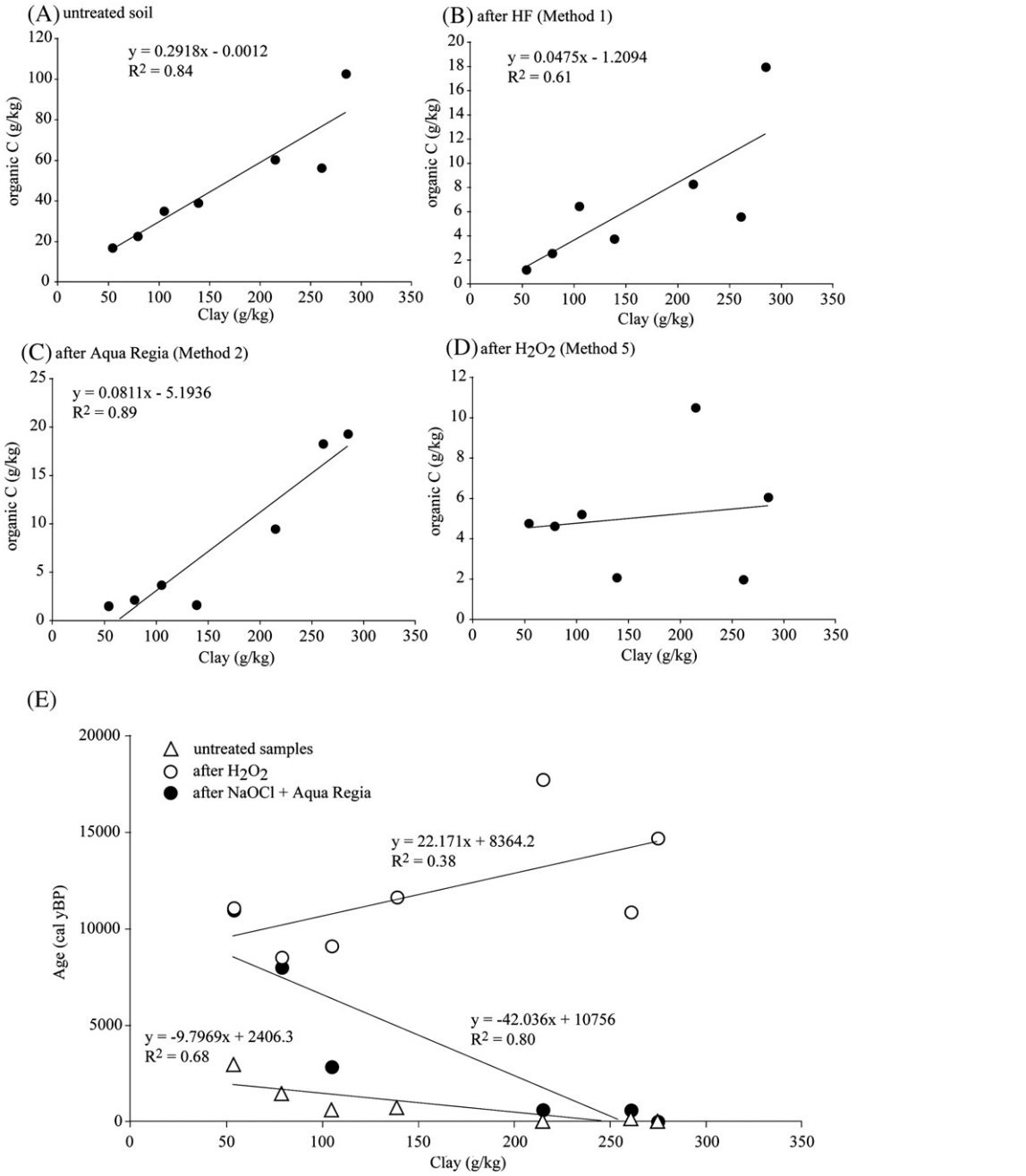

Fig. 5. Correlation between the organic C before and after the treatments (method 1, 2 and 5) and the clay content (A–D). The organic C content was recalculated using the recovery values. The measured ^{14}C ages (calibrated) of SOM in untreated samples, samples treated with NaOCl and Aqua Regia (method 4) and samples treated with H_2O_2 (method 5) are compared in (E).

treatment, a positive correlation of SOM with the clay fraction was found after each treatment. The clay content correlated with the ^{14}C age, i.e. the higher the clay content the lower was in general the age of the remaining SOM (Fig. 5). Such a trend was evident after each treatment, except for the H_2O_2 method. The more organic C is present in the soil, the more fresh material therefore adsorbs onto surfaces (Fig. 6). Methods 1–4 were consequently not able to completely eliminate this young material. Only in soil horizons with a low C content, i.e. in the subsoil, the destruction of young SOM material was effective enough to give rise to very high ^{14}C ages. The pMC of the removed OM correlated positively with the clay fraction and the SOM content after each treatment (Fig. 7), except with the H_2O_2 technique and the usage of NaOCl as the first treatment step. The oxidation with either NaOCl or H_2O_2 removes primarily young OM. Hypochlorite was, however, not efficient enough to remove all labile C. The higher the OM concentration in the soil, the more labile C was removed by HF and aqua regia (Fig. 7).

In untreated soils, nitrogen did not correlate very well with the clay fraction. This relationship was better after the treatments (except after H_2O_2). N-containing components were obviously more resistant to the treatments and were partially protected by clays and/or oxyhydoxides.

No or negative correlations were found between the SOM of untreated samples and SOM after the individual treatments and Fe–Al mineral phases. Only method 3 gave a positive correlation between the HF-extracted amount of SOM with oxyhydroxides. HF was

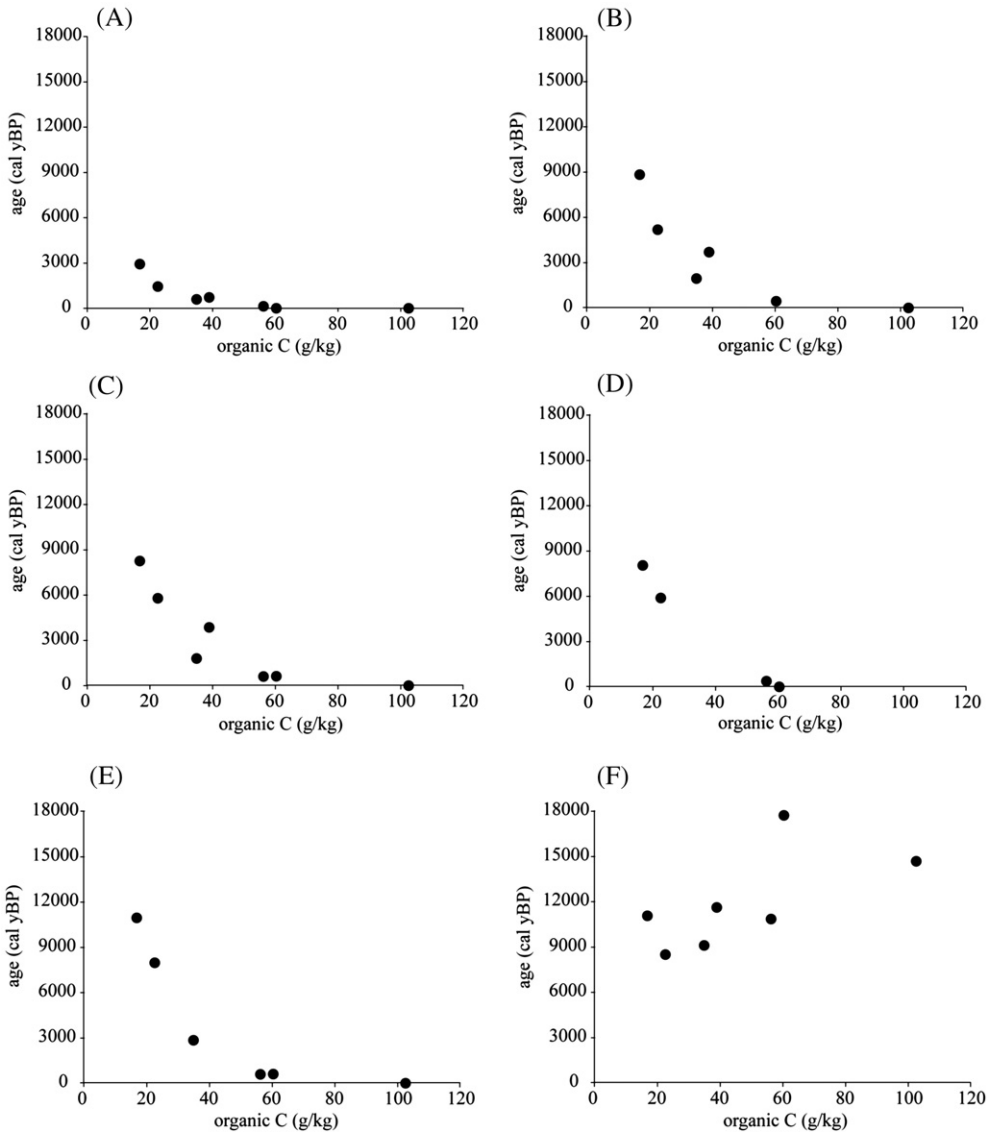

Fig. 6. Relationship between the content of soil organic C and the calibrated ^{14}C ages obtained with the individual treatment techniques. (A) untreated samples, (B) method 1 (NaOCl+HF), (C) method 2 (NaOCl+Aqua Regia), (D) method 3 (HF+NaOCl), (E) method 4 (Aqua Regia+NaOCl), (F) method 5 (H_2O_2).

obviously able to release additional organic matter by destroying oxyhydroxides.

4. Discussion

The methods that included HF (1 and 3) treatment led, in general, only to a small decrease in OM which agrees well with findings of other authors (i.e. Schmidt and Gleixner, 2005; Eusterhues et al., 2007). The overall loss in weight was, however, greatest using HF due to the dissolution of silicate minerals. Purification of SOM using HF includes the partial breakdown of Si–O bonds leading to the solubilisation of silicate minerals (Rumpel et al., 2006). HF and aqua regia have different strengths in breaking such bonds which explains the different weight of the samples after the treatments. The differences between the HF or aqua regia procedure (methods 1 and 2) were in general small with respect to the OM fractions and ^{14}C ages. The changed order of the reagents showed that aqua regia was, in contrast to HF, a more powerful reagent to eliminate organic matter leaving behind a resilient older fraction. The H_2O_2 treatment (method 5) was the most efficient method in isolating stable OM. This is in agreement with the results of Helfrich et al. (2007). Independent of the org. C concentration, H_2O_2 removed the easily degradable and, thus, labile OM fraction. N-containing compounds were less affected by oxidation. The other methods (methods 1–4) partially destroyed the old organic fraction and, consequently, gave rise to lower ages of the resistant fractions. Especially in the topsoil, where a high amount of organic matter was found, considerable proportions of young SOM remained unaffected using methods 1–4. The high concentrations of org. C in the topsoil obviously hindered an effective dissolution of minerals and the subsequent oxidation. The subdivision of organic matter into a labile, mineral-protected and recalcitrant fraction using the NaOCl and HF method produces, therefore, many uncertainties and is far from being precise.

According to the obtained results, the ^{14}C ages increased in the order: untreated samples < method 3 (HF+NaOCl) ≤ method 1 (NaOCl+HF) ≈ method 2 (NaOCl+aqua regia) < method 4 (aqua regia+NaOCl) < method 5 (H_2O_2).

Except for the H_2O_2 method, a negative correlation was found between the OC content and the ^{14}C age. The higher the content of SOM, the lower was the determined age (Fig. 6). This is in agreement with the results of Rumpel et al. (2002). They presumed young carbon to be located in horizons having a high carbon content. Only in the subsoil or in horizons having a low organic C concentration, was NaOCl (methods 1–4) effective enough in removing soil OC with a

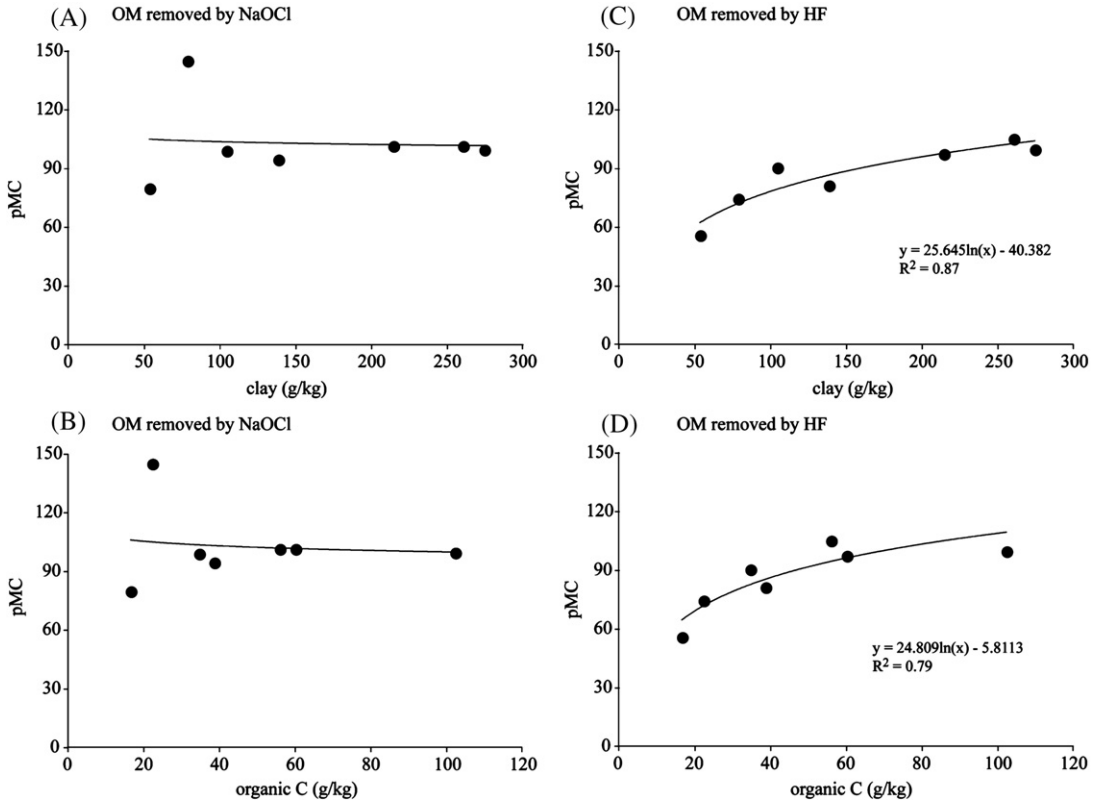

Fig. 7. Relationship between the pMC value (percent of modern carbon) of organic matter removed by NaOCl (method 1) and the clay content (A) and the soil organic C content (B). The relationship between the removed organic matter by HF (method 1) and the clay and the soil organic C content is given in (C) and (D), respectively.

relatively short residence time, leaving behind a more stable fraction (Kleber et al., 2005; Mikutta et al., 2006). In contrast, H_2O_2 was able to oxidise all labile OM and to isolate old and stable organic matter from soils having a high organic C content.

Calibrated radiocarbon ages of the treatment-resistant fraction of methods 1–4 showed an increase with soil depth in both profiles which agrees well with results from other authors (e.g. Rumpel et al., 2002; Mikutta et al., 2006). The first oxidation process step leaves behind intrinsically resistant organic materials (Theng et al., 1992; Cuypers et al., 2002). In contrast to all other methods, the highest ages of SOM after the treatment with H_2O_2 were measured in the topsoil. Young, contemporary carbon is transported by percolation in highly acidic soils via root growth, animal transport and through soil turbation processes such as cryoturbation, bioturbation, downward peloturbation, thus also contributing to the rejuvenation of the subsoil (Scharpenseel and Becker-Heidmann, 1992; Rumpel et al., 2002). Most of the modern carbon is less than 100 years old and decreases exponentially with increasing depth leading to an increase of the percentage of old carbon present (O'Brien and Stout, 1978; Mikutta et al., 2006). In the investigated Alpine soils (Holocene/Pleistocene), 3–15% of SOM in the surface horizons must be attributed to a very old OM fraction obtained after the H_2O_2 treatment. Although the proportion of this fraction increases with soil depth – which would fit with the findings of O'Brien and Stout (1978) – its mean age decreases. This trend would in theory, however, fit with theoretical expectances. Soil formation starts at the surface and proceeds with time to greater depths. Organic matter from plants and animals is incorporated into soil material and mixed with the mineral fraction. Because the investigated soils are podzols and consequently have a low biological activity and no earthworms, the ages of the old and stable SOM with increasing soil depth should decrease. Humic compounds may contract close and strong associations with the mineral phase, especially with clay minerals (Righi and Meunier, 1995). Clay organic complexes, once formed, do not easily exchange the organic component with infiltrated younger humus components (Scharpenseel and Becker-Heidmann, 1992; Fig. 5). In the investigated soils, some of the initially formed OM seems still to be present and detectable using the H_2O_2 treatment.

Using methods 1 to 4, a lower C/N ratio was found in the subsoil where most probably N-rich compounds interact with the mineral phase. Stabilisation of soil organic matter in soils is predominantly due to its interaction with mineral phases. According to Kleber et al. (2007) interaction occurs with polar organic functional groups of amphiphiles via ligand exchange with singly coordinated mineral hydroxyls to form stable inner-sphere complexes, proteinaceous materials adsorbed on charged surfaces ("contact" zone; Kleber et al., 2007) and association of hydrophobic substances with noncharged mineral surfaces ("zone of hydrophobic interactions"; Kleber et al., 2007). The higher C/N ratio of the resistant organic matter in the topsoil after methods 1 to 4 indicates that N-rich material was preferentially digested which would agree with results of Schmidt and Gleixner (2005) who noted a preferential loss of N over C during the HF treatment. Either N-rich organic matter that is strongly bound to clay minerals (= organic fraction of the "contact zone"; Kleber et al., 2007) or fresh material from the outer region (kinetic zone according to Kleber et al. (2007)) was eliminated. Because NaOCl was not efficient enough to remove all young OM, we must assume that HF and aqua regia also removed relatively easily degradable N-rich compounds from the outer zones (discrete zonal model according to Kleber et al., 2007).

The relative distribution of organic functional groups changed only slightly from the untreated to the NaOCl-treated and HF-treated soils (Fig. 2; highest proportion of C═O stretching of amide groups). This means that the treatments did not preferentially attack some specific functional groups or components. Methods that include aqua regia led to a relative enrichment of aliphatic and aromatic compounds. Furthermore, the oxidation- and aqua regia-resistant organic matter

fraction was enriched in N when compared to the untreated samples (Table 5). Similarly, the H_2O_2 treatment led to a resistant fraction which had not only a distinctly higher aliphatic content, but also more aromatic functional groups. The aromatic groups are indicative of charcoal-like substances. Several authors (e.g. Cheshire et al., 2000; Eusterhues et al., 2005) found oxidation-resistant organic matter enriched in aliphatic C and N containing compounds. Aliphatic material can be refractory in nature (e.g., fatty acids, waxes) and can bind to minerals by a variety of mechanisms. Specifically, the alkyl chain interacts with hydrophobic parts of the mineral matrix via van der Waals forces, whereas the carboxylic, alcoholic or amino functional groups may form hydrogen, ionic or coordination bonds with polar sites on mineral surfaces (Deng and Dixon, 2002). In addition, aliphatic compounds are believed to penetrate the interlayer space of expandable phyllosilicates at low pH (Theng, 1974).

The HF method partially destroyed mineral surfaces and consequently liberated strongly adsorbed N-rich compounds, while aqua regia affected the minerals less and did not liberate that many N-rich compounds. The H_2O_2 treatment (method 5) was the most efficient method in eliminating organic matter. After treatment, a N-rich and aliphatic organic fraction remained in the soil — in every horizon. The low C/N ratio after treatment does not, however, necessarily confirm that stabilisation of the H_2O_2-resistant soil organic matter is only due to its interaction with mineral phases. As the residual fraction (after treatment) did not show a good correlation with the clay content, we must assume that also refractory organic material exists with almost no interaction with minerals. Charcoal fragments which were not dissolved by H_2O_2 and were detected with SEM must therefore have a high age and be very stable. The other methods (methods 1–4) partially destroyed and mixed this old fraction with younger ones.

The FT-IR analyses confirmed the dissolution of kaolinite and other silicates with HF (Fig. 3). After the HF treatment, the peaks in the band region 650 cm^{-1} and near 515 cm^{-1} had, however, a higher intensity (Fig. 3). These peaks (Anghel et al., 1999) are typical for the mineral cryolite (Na_3AlF_6). Cryolite was obviously formed during the HF treatment by a reaction between Al and Na (deriving from minerals) and F from HF. The precipitation of Al–F-phases could also have caused a co-precipitation of (young?) SOM which probably influenced the age of the resilient organic matter.

All methods used gave a higher age for the soil from Rabbi 38 than that from Lax 1. This was also confirmed by the higher evolutional status of the former with a more expressed podzolisation (i.e. expressed by the differences between subsoil and surface horizon regarding Al_o, Al_d and Fe_o). There is a good agreement with the age obtained from the dating of charcoal and H_2O_2-resistant organic matter in soil profile Lax 1. The soil age derived from charcoal gives 10,700 cal BP and the one derived from OM (H_2O_2 resistant) 10,851 cal BP. This age corresponds well with the end of the Egesen-equivalent glacial state (Maisch et al., 1999; Kerschner, 2000) or the early Preboreal. Soil formation could have started approximately 11,000 yBP. The soil profile Rabbi 38 would consequently have an age of 17,729 cal BP (oldest age of the H_2O_2-resistant OM fraction). This age fits to the documented deglaciation which occurred worldwide and to the oldest Dryas when moraines of the Gschnitz-, Senders- and Daun-equivalents were deposited (Maisch et al., 1999). Lax 1 is on a moraine within a glacial cirque where a small, Alpine glacier probably re-advanced during the Egesen-equivalent. Rabbi 38, however, seems to be on an older part of the moraine which most probably became ice-free after the decay of the main valley-glacier. Consequently, the morphological position of the soil profiles supports the findings of the dating.

Helfrich et al. (2007) obtained very large ages for SOM when using H_2O_2 or $Na_2S_2O_8$. The ^{14}C age of the H_2O_2-resistant organic matter from soils developed on loess was in the range of 13,000 yBP, which would correspond to a calibrated age of around 16000 yBP. These authors suggested that some of the old, stable SOC was already present in the loess deposit and was thus not formed in situ. The measured age would, however, fit quite well with the Lateglacial when loess was deposited.

5. Conclusions

We tested five different methods to extract the oldest possible organic matter that potentially could be used as a tool for dating soils or the start of soil formation. Methods 1 and 2 consisted of a NaOCl oxidation followed by a treatment with either HF or aqua regia. In methods 3 and 4, the order of the treatments was changed with the application of HF or aqua regia as the first step and the oxidation with NaOCl as the second. In method 5, only H_2O_2 was used. We obtained the following main findings:

- the H_2O_2 treatment leaves behind an organic fraction having the highest ages.
- in contrast to the other methods, the highest ^{14}C age was measured in the topsoil using H_2O_2.
- the treatments using aqua regia gave similar results to that using HF with respect to the ages and size of the different organic matter pools. HF is a dangerous reagent and can probably be substituted by aqua regia, at least when Alpine soils developed on a silicate parent material are investigated.
- the changed order of the NaOCl and HF/aqua regia treatments produced only different results for aqua regia, where higher ages were obtained using aqua regia as the first step. Reversal of HF and NaOCl treatments gave identical results.
- methods 3 and 4 leave behind an N-richer OM after the treatment and, in general, higher ages than methods 1 and 2.
- NaOCl is too weak a reagent to oxidise all labile organic matter in soils. It seems to work more or less properly only in soils with a low OC content.
- the use of HF (in method 1) produced artefacts (precipitation of cryolite). This could also influence organic matter (co-precipitation) and finally its age.
- HF treatment destroyed kaolinite, attacked quartz but did not affect that much other phyllosilicates (like mica).
- the subdivision of organic matter into a labile, mineral-protected and recalcitrant fraction using the NaOCl and HF method produces many uncertainties and is far from being precise. A clear separation of these SOM fractions is not possible when the soils have a large content of organic matter.
- clay minerals protect OM from degradation. There is, however, a high competition for adsorption places of OM in surface soils. According to our results, we propose the following conceptual model for resilient OM: one part of OM seems to be very strongly fixed to (clay) minerals and almost no exchange with the surrounding environment occurs. In addition, a strongly recalcitrant OM must be present probably due to resistant charcoal that does not interact with the inorganic part of the soil.
- the application of HF or aqua regia destroyed most probably a part of the strongly fixed OM. H_2O_2, however, is able to remove the younger fractions without affecting the oldest one. The isolated pool of organic matter after the H_2O_2 treatment is an inert fraction of SOM with a mixture of charcoal and organic materials strongly adsorbed on or trapped in clays (see Frink, 1995; Skjemstad et al., 1996; Falloon et al., 1998).
- the H_2O_2 treatment seems to enable the dating of undisturbed Holocene/Pleistocene-aged soils. This has, however, to be confirmed with additional absolute dating techniques such as exposure dating of rock surfaces with ^{10}Be and ^{26}Al.

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Manuscript II

Combination of numerical dating techniques using ^{10}Be in rock boulders and ^{14}C in resilient soil organic matter for reconstructing glacial and periglacial processes in a high Alpine catchment during the late Pleistocene and early Holocene

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COMBINATION OF NUMERICAL DATING TECHNIQUES USING ^{10}Be IN ROCK BOULDERS AND ^{14}C OF RESILIENT SOIL ORGANIC MATTER FOR RECONSTRUCTING THE CHRONOLOGY OF GLACIAL AND PERIGLACIAL PROCESSES IN A HIGH ALPINE CATCHMENT DURING THE LATE PLEISTOCENE AND EARLY HOLOCENE

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ABSTRACT. Glacier fluctuations and paleoclimatic oscillations during the Late Quaternary in Val di Rabbi (Trentino, northern Italy) were reconstructed using a combination of absolute dating techniques (^{14}C and ^{10}Be) and soil chemical characterization. Extraction and dating of the stable fraction of soil organic matter (SOM) gave valuable information about the minimum age of soil formation and contributed to the deciphering of geomorphic surface dynamics. The comparison of ^{10}Be surface exposure dating (SED) of rock surfaces with the ^{14}C ages of resilient (resistant to H_2O_2 oxidation) soil organic matter gave a fairly good agreement, but with some questionable aspects. It is concluded that, applied with adequate carefulness, dating of SOM with ^{14}C might be a useful tool in reconstructing landscape history in high Alpine areas with siliceous parent material. The combination of ^{14}C dating of SOM with SED with cosmogenic ^{10}Be (on moraines and erratic boulders) indicated that deglaciation processes in Val di Rabbi were already ongoing by around 14,000 cal BP at an altitude of 2300 m asl and that glacier oscillations might have affected the higher part of the region until about 9000 cal BP. ^{10}Be and ^{14}C ages correlate well with the altitude of the sampling sites and with the established Lateglacial chronology.

INTRODUCTION

Clear evidence of distinct climatic conditions, such as moraines and rock glaciers, make high mountain areas unique archives of past climate change effects on landscape dynamics. Since the initial work of Penck and Brückner (1901/1909) on Alpine glaciations and the structure of glacier retreat at the end of the last glaciation (the Würmian), numerous authors have worked on ice-age glacial stratigraphy (e.g. Keller and Krayss 1987, 2005; Schlüchter 1988, 2004), on the Lateglacial ice decay (e.g. Maisch 1981, 1987; Schoeneich 1999; Kerschner et al. 1999; Ivy-Ochs et al. 2004, 2006a,b, 2007), and also in detail on Holocene glacier fluctuations in the Alps (e.g. Holzhauser 1984; Hormes et al. 2001; Holzhauser et al. 2005; Joerin et al. 2006, 2008). While the general sequence and the related morphostratigraphic positions of the various stadials are quite widely accepted, reliable dating exist only for a few of them (Heitz et al. 1982; Maisch 1987; Schlüchter 1988; Kerschner et al. 1999; Ivy-Ochs et al. 2006a,b, 2007, 2008). This lack of direct dating reflects the various limitations of the applied dating methods and the rareness of optimal sampling sites (representative of the investigated site). The link between distinct moraine sequences and the absolute timescale is still highly speculative, especially in the central Eastern Alps. The timescales of the formation of the landscape reach as far back as the alpine orogeny, but mainly relate to the Lateglacial ice retreat at the end of the last Ice Age (20,000–11,500 yr BP) and include also the entire Holocene period. The Alpine area offers interesting geomorphological settings with pronounced glacial and periglacial features, such as Lateglacial moraines, erratic boulders, and rock glaciers, that give the opportunity to date the retreat stages of the glaciers and to investigate the subsequent geomorpho-

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logical modifications during the Holocene. Surface exposure dating (SED) is based on the *in situ* production and accumulation of cosmogenic nuclides (e.g. ^{10}Be, ^{26}Al, ^{36}Cl) within the first few decimeters of an exposed rock surface (Lal 1991; Gosse and Phillips 2001). This accumulation is used to determine the elapsed time since the rock surface was first exposed to cosmic rays (Nishiizumi et al. 1989; Gosse and Phillips 2001). Hence, the deposition age of boulders in various topographical situations can be measured. Several studies have shown that SED is an innovative and powerful tool for the reconstruction of glacial and climate history (e.g. Gosse et al. 1995; Ivy-Ochs et al. 2004; Briner et al. 2005; Schaefer et al. 2006). In order to compare the magnitude and timing of former glacier extents, absolute dating methods can be applied and compared to determine the age of particular glacial stages and—in combination with other approaches, i.e. by paleoglaciological reconstructions (equilibrium line altitude [ELA] depressions)—the paleoclimatic signal they represent (Kelly et al. 2004; Kerschner and Ivy-Ochs 2008).

Soils can provide useful information for the geomorphological interpretation of mountainous terrain. Their spatial distribution in Alpine areas reflects the impact of the soil-forming factors, and once their influence is known, soils can help to introduce additive aspects of landscape evolution that otherwise may be left undetected (Birkeland et al. 2003). The dating of soil organic matter (SOM) with ^{14}C is well suitable, if humified and stable substances that were produced almost at the beginning of soil formation can be found and dated, giving the possibility to elucidate soil dynamic processes (Scharpenseel and Becker-Heidmann 1992).

The main aim of the study was to test and compare signals of landscape evolution obtained from soils developed on moraines using radiocarbon ages from stable organic matter with SED obtained from rock boulders. For this purpose, we investigated 4 soils developed on morainic and glacial substrata (paragneiss) with respect to their chemical composition and to the ^{14}C ages of the most stable resilient organic material (e.g. Eusterhues et al. 2005; Mikutta et al. 2006). In the vicinity of the studied soils, we sampled 4 erratic boulders (>2 m^3, in stable position) located on lateral moraines for ^{10}Be surface exposure dating (SED). The comparison between the ^{14}C and ^{10}Be method enabled to test the validity of the dating technique using resilient SOM. The combination of ages derived from ^{10}Be and ^{14}C dating should, furthermore, give insights into the deglaciation processes and the climatic fluctuations occurring during the late Pleistocene and early Holocene in the central-eastern Alps in Italy.

SITE DESCRIPTION

The investigation area is located in Val di Rabbi, in a small side cirque within a lateral valley of Val di Sole, Trentino, in the southern Alpine belt of northern Italy (Figure 1). The climate of the valley ranges from temperate to alpine (above the timberline). Mean annual temperatures range from 8.2 °C (valley floor, at ~800 m asl) to around 0 °C (at 2400 m asl) and mean annual precipitation approximately from 800 to 1300 mm/yr (Servizio Idrografico 1959). The timberline is close to 2100–2200 m asl and the forests are dominated by the conifers *Larix decidua* and *Picea abies* (Pedrotti et al. 1974). Areas above 2300 m are covered with rocks, boulders, and short-grass meadows dominated by *Carex curvula* and *Nardus stricta*.

The 4 investigated soils and boulders (Figure 1; Tables 1 and 2) are located between 2100 and 2456 m asl, hence, close to the timberline and in the high alpine zone (Figure 1, Tables 1 and 2). The soil types were Entic Podzol and Haplic Podzol at lower altitudes (between 2000 and 2200 m asl) and Protospodic Leptosol and Brunic Regosol developed at around 2300 m asl according to the WRB (IUSS Working Group 2006). According to the soil taxonomy (Soil Survey Staff 2006), the soil moisture regime is udic (humid conditions, <90 days/yr with a dry soil) at all sites and the soil

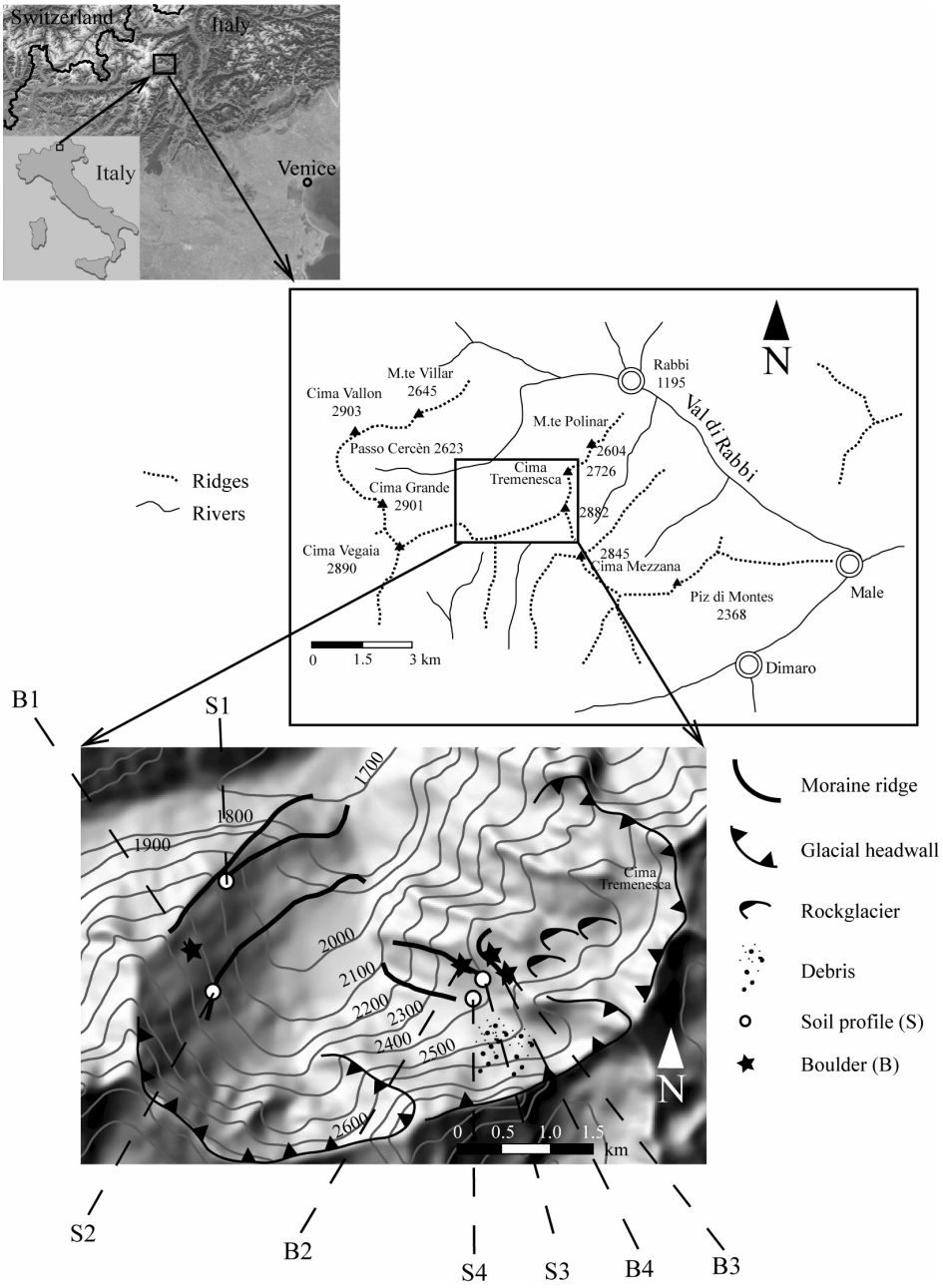

Figure 1 Location of the investigation site, soil profiles, rock boulders (S = soil profile; B = boulder) and main geomorphologic features.

temperature regime is cryic (mean annual temperature <8 °C, without permafrost). Soil material was collected from excavated pits, and undisturbed soil samples were taken, where possible, down to the BC or C horizon (parent material). Two to 4 kg of soil material were collected per soil horizon from the 4 soil pits (Hitz et al. 2002). The landscape near the investigation sites was strongly influenced by former glaciers and the sampled soils developed on moraines or on rock glaciers (paragneiss)

Table 1 Characteristics of the investigated soils.

Profile	Elevation (m asl)	Aspect (°N)	Slope (%)	Parent material	Vegetation	WRB (IUSS Working Group 2006)
S1	2100	60	32	Paragneiss morainic material	*Larix decidua*/*Juniperus communis*	Entic Podzol
S2	2230	70	55	Paragneiss morainic material	*Rhododendro-vaccinietum extrasilvaticum*	Haplic Podzol
S3	2380	320	5	Paragneiss morainic material	*Carex curvula*/*Nardus stricta*	Protospodic Leptosol
S4	2370	300	10	Paragneiss, inactive rock glacier/solifluction	*Carex curvula*/*Nardus stricta*	Brunic Regosol

being inactive today. According to the geomorphological studies of Baroni and Carton (1990) and Filippi et al. (2007), surface ages were estimated to 14,000–16,000 yr. Large lateral moraines extend down to 1700–2000 m asl and glacial deposits, such as erratic boulders, can be found up to 2600 m asl. Big boulders (>2 m^3) with prominent quartz veins in flat and stable positions are widespread throughout the investigated area.

METHODS

Soil Chemistry and Physics

The soil samples were air-dried; large aggregates were gently broken by hand and sieved to <2 mm. Total C and N contents of the soil were measured with a C/H/N analyzer (Elementar Vario EL, Elementar Analysensysteme GmbH) using oven-dried (105 °C) and ball-milled fine earth. Total C corresponds in our case to organic C due to the absence of any carbonates in the soil. Soil pH (in 0.01M $CaCl_2$) was determined on air-dried samples of the fine earth fraction using a soil solution ratio of 1:2.5. After a pretreatment of the samples with H_2O_2 (3%), particle size distribution of the soils was measured by a combined method consisting of sieving the coarser particles (2000–32 μm) and measurement of the finer particles (<32 μm) by means of an X-ray sedimentometer (SediGraph 5100). The dithionite- (Fe_d, Al_d) and oxalate-extractable (Fe_o, Al_o) iron and aluminium fractions were extracted according to McKeague et al. (1971) and analyzed by AAS (atomic absorption spectrometry—AAnalyst 700, PerkinElmer, USA)

Extraction of the Stable Organic Matter (SOM)

Acting on the assumption that chemical oxidation mimics natural oxidative processes, we treated the soils with 10% H_2O_2 to eliminate the more labile organic material from the more refractory organic matter (Plante et al. 2004; Eusterhues et al. 2005; Mikutta et al. 2006; Helfrich et al. 2007). The stable fraction that remained at the end of the treatment was supposed to be part of the first organic matter formed in the sediment after glacier retreat (Favilli et al. 2008) and to provide minimum ages of deposition of the moraines and of deglaciation. One gram of air-dried soil was wetted for 10 min with a few mL of distilled water in a 150-mL beaker. Afterwards, 90 mL of 10% H_2O_2 were added. The procedure was run at a minimum temperature of 50 °C throughout the treatment period. The beakers were closed with 2 layers of parafilm to avoid evaporation of the reagent. Peroxide treatments were performed for 168 hr (7 days). At the end of the treatment, the samples were washed 3 times with 40 mL deionized water, freeze-dried, weighed, analyzed for total C and N, and ^{14}C dated.

Radiocarbon Dating

The CO_2 of the combusted samples was catalytically reduced over cobalt powder at 550 °C to elemental carbon (graphite). After the reduction, this mixture was pressed into a target and the ratios ^{14}C:^{12}C (for ^{14}C age) were measured by accelerator mass spectrometry (AMS) using the tandem accelerator of the Institute of Particle Physics at the Swiss Federal Institute of Technology Zürich (ETHZ). The calendar ages were obtained using the OxCal 4.0.5 calibration program (Bronk Ramsey 1995, 2001) based on the IntCal04 calibration curve (Reimer et al. 2004). Calibrated ages are given in the 2-σ range (minimum and maximum value).

Exposure Dating

Four large boulders on top of moraines with volumes >2 m^3 were sampled for exposure dating. The assumption is that boulders were transported by glaciers during the last glaciation and were, since the time of the last glacier retreat, exposed to cosmic rays without being moved from their present position. Gosse et al. (1995) demonstrated that on a single alpine moraine the cosmogenic nuclide ages reflect the timing of deposition. According to the position of the selected boulders in the investigation area, it is not likely that they were pre-exposed to cosmic rays before being deposited by the glacier. Similarly, based on results from numerous sites in the Alps, we consider pre-exposure extremely unlikely (Ivy-Ochs et al. 2007). These boulders were chosen for dating in order to exclude any long-term effects from slope-movement processes (Table 2). Rock samples were crushed, sieved, and leached in order to obtain pure quartz following Kohl and Nishiizumi (1992) and Ivy-Ochs (1996). ^{9}Be solution was added to the dried quartz, which was then dissolved in 40% HF. Be was isolated using anion and cation exchange columns followed by selective pH precipitation techniques (Ivy-Ochs 1996). $^{10}Be/^{9}Be$ ratios were measured at the ETH AMS facility. The surface exposure ages listed in Table 2 were calculated using a sea-level high-latitude production rate of 5.1 ± 0.3 (^{10}Be atoms/g SiO_2/yr) with 2.2% production due to negative muon capture (Stone 2000). This production rate was scaled for latitude (geographic) and altitude (Stone 2000) and corrected for sample thickness assuming an exponential depth profile, a rock density of 2.65 g cm^{-2} (quartz veins), and an effective collimated radiation attenuation length of 155 g cm^{-2} (Gosse and Phillips 2001). Topographic shielding was based on a zenith angle dependence of $(\sin\theta)^{2.3}$ (Dunne et al. 1999). The errors given for each boulder age reflect the analytical uncertainties of the AMS measurement parameters. The exposure age was corrected for mean snow cover (Gosse and Phillips 2001) with an assumed snow density of 0.3 g cm^{-3}. The duration of the snow cover (6 months, Table 2) was estimated according to Auer et al. (2003) from climatic data supplied by the Provincia Autonoma di Trento (Dipartimento Protezione Civile e Tutela del Territorio, Ufficio Previsioni e Organizzazione). In our case, the snow correction increased the exposure ages significantly. A geomagnetic field correction (Pigati and Lifton 2004) was omitted because its possible effect is small (1–2%).

RESULTS

Chemical Composition and Physical Characteristics of the Soils

The investigated soils are characterized by a high proportion of rock fragments ranging from 0 up to 60% of the total weight (Table 3). These are typical values for alpine soils on a moraine type substratum (Egli et al. 2001). All investigated soils have a sandy to silty-sandy texture. The proportion of sand decreased towards the soil surface, and correspondingly silt and clay increased (Table 3). The decrease of the grain sizes from the bottom to the top of the soil profile is a clear effect of weathering. Due to the siliceous parent material, the soils show pronounced acidification (Table 4). Eluviation and illuviation of Fe and Al is typical for the podzolized soils (S1 and S2). A distinct increase

Table 2 List of samples for surface exposure dating, elevation and latitude of the sample sites, thickness of sample, dip (angle from horizontal) of the surface sample, amount of quartz retrieved from the sample that was used for the measurement of ^{10}Be, correction factor for topography, production rate, ^{10}Be measured concentration in the sample, measurement error, and ^{10}Be date.

Sample	Elevation (m asl)	Lat. (°N)	Long. (°E)	Sample thickness (cm)	Surface dip (°)	Direction of dip (°)	Shielding corr.	Depth corr.	Snow cover[a] (m)	Local prod. rate (at g^{-1} yr^{-1})	^{10}Be[b] (at g^{-1} [1E+5])	Error[c] (%)	^{10}Be date (yr)	^{10}Be date (snow corr.) (yr)
B1 (W67)	2247	46.3763	10.7697	3	30	270	0.931	0.975	1.3	27.70	3.23	10.1	11,680 ± 1180	13,230 ± 1340
B2 (W70)	2360	46.3736	10.7883	5	38	270	0.927	0.958	0.7	29.27	3.24	8.5	11,110 ± 940	11,620 ± 990
B3 (W72)	2456	46.3747	10.7911	5	30	220	0.961	0.958	0.3	32.34	3.15	7.9	9780 ± 770	9920 ± 780
B4 (W73)	2446	46.3750	10.7902	5	16	240	0.982	0.958	0.3	32.84	2.85	7.8	8710 ± 680	8840 ± 690

[a]Average value of snow cover during 6 months.

[b]Using ETH AMS standard S555 (^{10}Be/^{9}Be = 95.5 10^{-12} nominal) with a ^{10}Be half-life of 1.51 Myr.

[c]Estimated total error including measurement error and the effects of altitude, latitude and topography/depth scaling.

of dithionite and oxalate iron and aluminium is observed in all spodic horizons (Table 4). The soil S3 is rather shallow but showed the typical characteristics of a developing Podzol (Al, Fe, and organic C translocation within the soil profile and formation of a Bhs horizon). In the soil profile S4, no clear translocation of Fe and Al forms is detectable due to a lower stage of soil development. This soil developed in an area with former solifluidal activity. The soil has a polygenetic horizon sequence due to the accumulation of younger material on top of a former surface (Figure 2). The concentration of organic C in the profile shows a strong increase in the Ab horizon, thus confirming the macromorphological observation (Table 4).

Table 3 Physical characteristics of the investigated soils.

Site	Horizon	Depth (cm)	Munsell color (moist)	Skeleton[a] (%)	Sand (g/kg)	Silt (g/kg)	Clay (g/kg)
S1							
	AE	0–4	10YR 3/3	5	455	280	265
	BE	4–8	5YR 4/4	11	515	280	205
	Bs1	8–20	7.5YR 4/4	51	575	286	139
	Bs2	20–45	10YR 4/4	45	671	275	54
	BC	45–60	10YR 5/4	34	nd	nd	nd
S2							
	AE	0–9	7.5YR 2/1	3	397	398	205
	Bhs	9–20	7.5YR 3/3	19	717	209	74
	Bs	20–40	7.5YR 4/3	58	709	252	39
S3							
	AE1	0–4	10YR 2/3	8	457	223	320
	AE2	4–12	10YR 3/2	21	576	212	212
	Bhs	12–20	10YR 1.7/1	45	638	172	190
S4							
	A	0–8	10YR 3/2	0	352	496	152
	Bw1	8–20	10YR 4/4	1	409	437	154
	Bw2	20–32	10YR 4/4	32	692	258	50
	Ab	32–35	10YR 3/3	2	309	498	193
	Bb	35–40	10YR 4/4	49	839	136	25

[a]Size fractions: skeleton = >2 mm; sand = 2000–62 µm; silt = 62–2 µm; clay = <2 µm; nd = not determined.

Table 4 Chemical characterization of the investigated soils.

Site	Horizons	pH ($CaCl_2$)	Org. C (%)	Total N (%)	C/N	Al_o (g/kg)	Fe_o (g/kg)	Al_d (g/kg)	Fe_d (g/kg)
S1									
	AE	3.7	10.37	0.57	18	1.73	5.57	2.50	15.90
	BE	3.6	6.10	0.29	21	1.91	6.06	2.80	20.50
	Bs1	4.1	3.94	0.18	22	10.27	19.62	14.70	44.10
	Bs2	4.4	1.70	0.07	24	5.84	9.37	7.30	21.40
	BC	4.5	0.75	0.06	12	4.04	1.67	5.60	6.90
S2									
	AE	3.4	18.46	0.88	21	2.78	5.67	3.94	14.53
	Bhs	3.7	6.38	0.27	24	6.31	24.90	5.96	45.33
	Bs	4.15	2.54	0.12	21	6.41	8.81	10.65	30.13
S3									
	AE1	3.4	12.49	0.68	18	2.03	2.47	2.80	8.50
	AE2	3.55	4.80	0.22	22	2.48	4.33	3.20	11.00
	Bhs	3.85	7.14	0.31	23	8.30	13.76	14.20	27.10

Table 4 Chemical characterization of the investigated soils. *(Continued)*

Site	Horizons	pH ($CaCl_2$)	Org. C (%)	Total N (%)	C/N	Al_o (g/kg)	Fe_o (g/kg)	Al_d (g/kg)	Fe_d (g/kg)
S4									
	A	3.85	5.53	0.38	15	3.05	7.05	5.40	21.90
	Bw1	4.00	2.07	0.15	14	2.47	9.61	5.00	30.80
	Bw2	4.1	1.95	0.13	15	1.58	4.21	3.30	20.60
	Ab	3.95	6.20	0.39	16	4.39	6.52	7.50	23.10
	Bbw	4.25	0.91	0.05	18	1.57	3.70	2.70	15.30

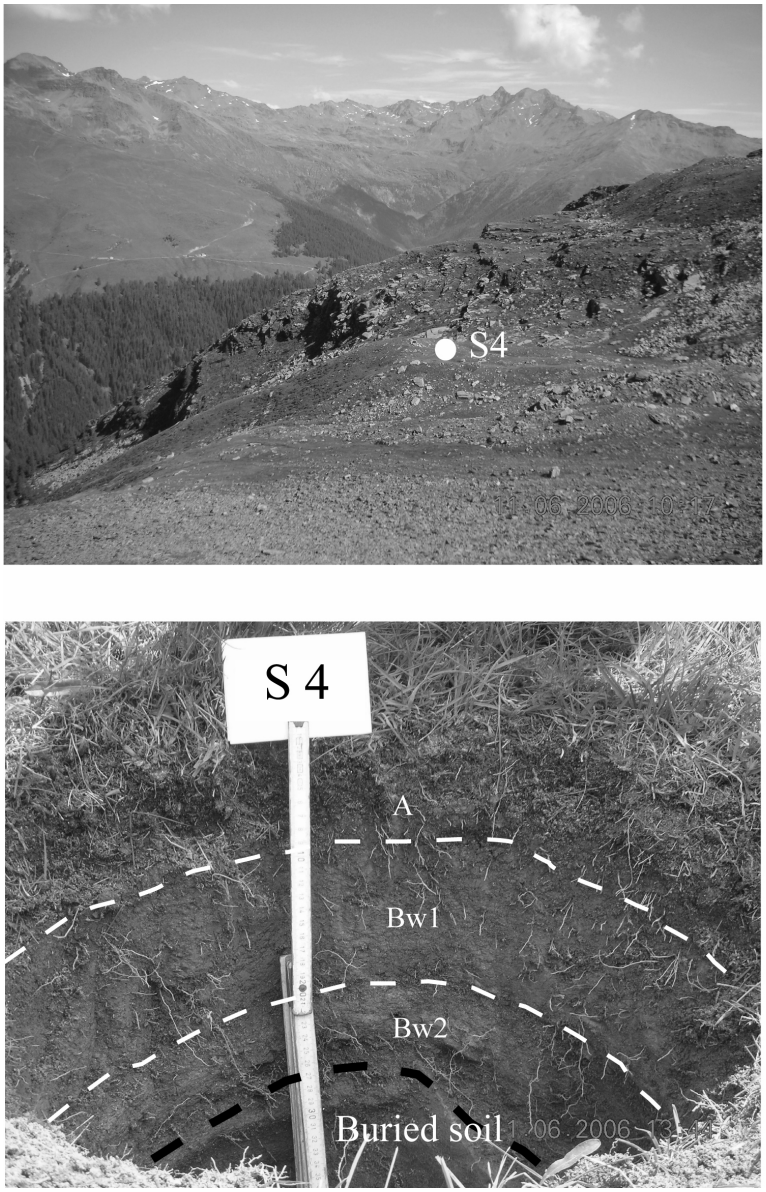

Figure 2 A) Location of the soil profile S4; B) Soil profile S4 with horizons and buried soil

Radiocarbon Age of Soil Organic Matter and ^{10}Be Age of Boulders

The ages of SOM varied considerably within all soil profiles (Table 5). The highest age of the H_2O_2-treated samples was usually measured in the E or B horizon (Bs or Bhs) and gives an indication about the start of soil formation. H_2O_2 is a strong reagent to oxidize all labile organic matter in soils (Favilli et al. 2008).

Table 5 Measured and calibrated ^{14}C ages of untreated and H_2O_2-treated soil samples. Calibrated ^{14}C ages are given in the 2-σ range.[a]

Site	Soil type, depth (cm)	Soil horizon	ETH # untreated	Uncal ^{14}C untreated	Cal ^{14}C untreated	ETH # H_2O_2-treated	Uncal ^{14}C H_2O_2-treated	Cal ^{14}C H_2O_2-treated
S1	**Entic Podzol**							
	0–4	AE	-33323	–650 ± 40	Modern	-33508	12,470 ± 90	14,160–14,964
	4–8	BE	-33324	–30 ± 40	Modern	-33509	14,410 ± 110	16,782–17,839
	8–20	Bs1	-33325	780 ± 40	666–772	-33510	10,060 ± 85	11,274–11,972
	20–45	Bs2	-33326	2815 ± 45	2794–3064	-33511	9735 ± 75	10,786–11,270
	45–60	BC	—	—	—	—	—	—
S2	**Haplic Podzol**							
	0–9	AE	—	—	—	-33972	2360 ± 50	2207–2699
	9–20	Bhs	—	—	—	—	—	—
	20–40	Bs	—	—	—	-33973	9775 ± 70	10,825–11,386
S3	**Protospodic Leptosol**							
	0–4	AE1	—	—	—	-33976	5115 ± 55	5729–5989
	4–12	AE2	—	—	—	—	—	—
	12–20	Bhs	-34208	650 ± 50	546–676	-33977	9425 ± 75	10435–11073
S4	**Brunic Regosol**							
	0–8	A	—	—	—	-33974	7655 ± 65	8370–8585
	8–20	Bw1	—	—	—	—	—	—
	20–32	Bw2	—	—	—	-35573	8025 ± 60	8647–9073
	32–35	Ab	-33978	2505 ± 50	2366–2743	-33975	11,920 ± 85	13,596–13,991
	35–40	Bbw	—	—	—	—	—	—

[a] — = not determined.

The measured lower ages in the AE horizon of profile S2 and the AE1 horizon of profile S3, compared to those of the subsoil, are most probably due to the very high C content and, therefore, either to the incapability of H_2O_2 to oxidize all young OM or to young OM, which was able to expel older C. The untreated soil organic matter from the whole top- and subsoil of site S3 (Table 5, Bhs horizon) seems to have in general a very young age. Strong leaching conditions, due to the very low pH, have caused the downward migration of soluble young-aged organic material compounds with soil percolating water into the subsoil. The H_2O_2 treatment, performed on the sample from the Bhs horizon, gave an age of 10,435–11,073 cal BP of the resilient OM fraction.

The ^{14}C results show that the site S4 has a polygenetic soil. Soil formation in the initial layer started around 13,596–13,991 cal BP and ended, due to the accumulation of eroded material (probably slope deposits), between 2366–2743 cal BP (Table 5). This burial event was inferred from dating root remains in the Ab horizon. The accumulation was probably due to periglacial activity/processes (solifluction) during a colder period around 2500 yr BP. This periglacial period would fit with the Göschener I cold phase, which occurred around 3.0–2.3 kyr (Zoller et al. 1966; Maisch et al. 1999; Figure 4). Preweathered sediments containing already organic material (having an age between 8370–9073 cal BP) were deposited on top of the original soil (horizon A/Bw2; Figure 2).

The ^{10}Be dates from the sampled boulders range from 13,230 to 8840 yr (Table 2). The ^{10}Be ages decrease with increasing altitude, which is in agreement with the general direction of retreat of the glaciers after the LGM (Last Glacial Maximum). The position of the boulders in the investigation area supports the calculated ages (Figures 1 and 5). If exposure ages and ^{14}C ages (start of soil formation) are plotted versus elevation, a significant (r^2 = 0.68; p = 0.0115), linear relationship is obtained (Figure 3).

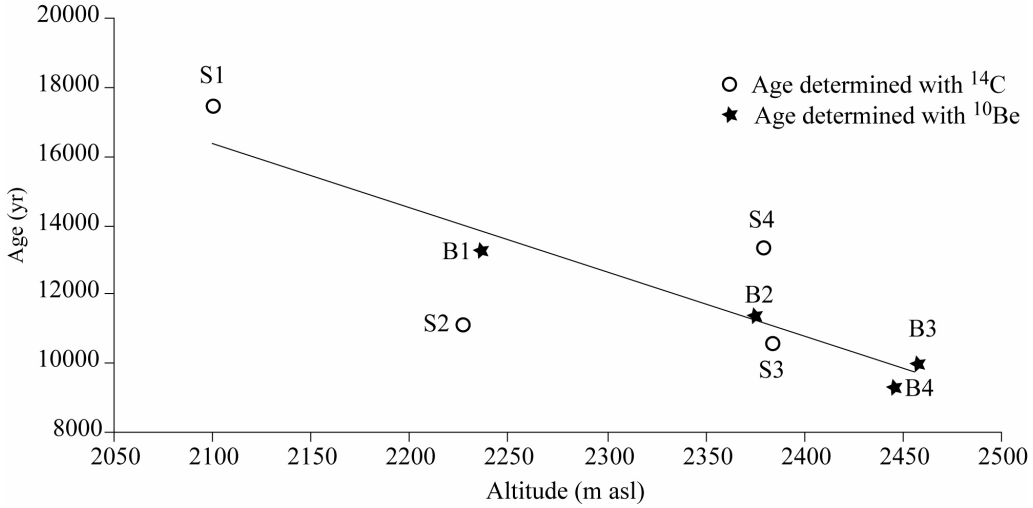

Figure 3 Relationship between the obtained ages (^{14}C [calibrated age] and ^{10}Be) and the elevation of the dated objects

The ^{14}C age of stable organic matter extracted from soil S1 implies that the oldest moraine (at an altitude of 2100 m asl) had already been deposited by around 16,782–17,839 cal BP (Figure 4, Table 5). The soil S4 at 2370 m asl started to develop 13,596–13,991 cal BP. More or less simultaneously, the boulder B1, located at 2247 m asl, was deposited on a moraine. Around 11,700 yr ago, the site B2 at 2360 m asl was affected by the re-advance of a small glacier tongue, most probably during the late Egesen glacial stage (Younger Dryas) or the early Preboreal (Ivy-Ochs et al. 2006a, 2008) with the deposition of new material (Figure 5). The soil S3, located a short distance from B2, started its evolution shortly after the deposition of the moraine. The chemical and morphological evolution of the soil profile S3 confirms that this soil has had an undisturbed development during the last 10,000 yr—a time span that leads to well-developed Podzols (e.g. Starr 1991; Barett and Schaetzl 1992; Lundström et al. 2000). The following period, the Holocene, was characterized by higher temperatures (Clapperton 1995), which finally caused the total disappearance of the glaciers in the investigation area. Periglacial activity (solifluction) was, however, traceable at the site S4 until around 2366–2743 cal BP. This soil profile is polygenetic and strongly influenced by solifluction (accumulation of soil material because of slope deposits, burial of a former soil) around that period.

DISCUSSION

The moraines in the study area are characterized by sharp crests and numerous large boulders (cf. Ivy-Ochs et al. 2006, 2008). The investigated soils are well developed and show the typical characteristics of podzolization, with the formation of an eluvial and a illuvial horizon. The oxidation of SOM with H_2O_2 left behind intrinsically resistant soil organic matter (Theng et al. 1992; Cuypers et al. 2002; Favilli et al. 2008). Humic compounds may form close and strong associations with the

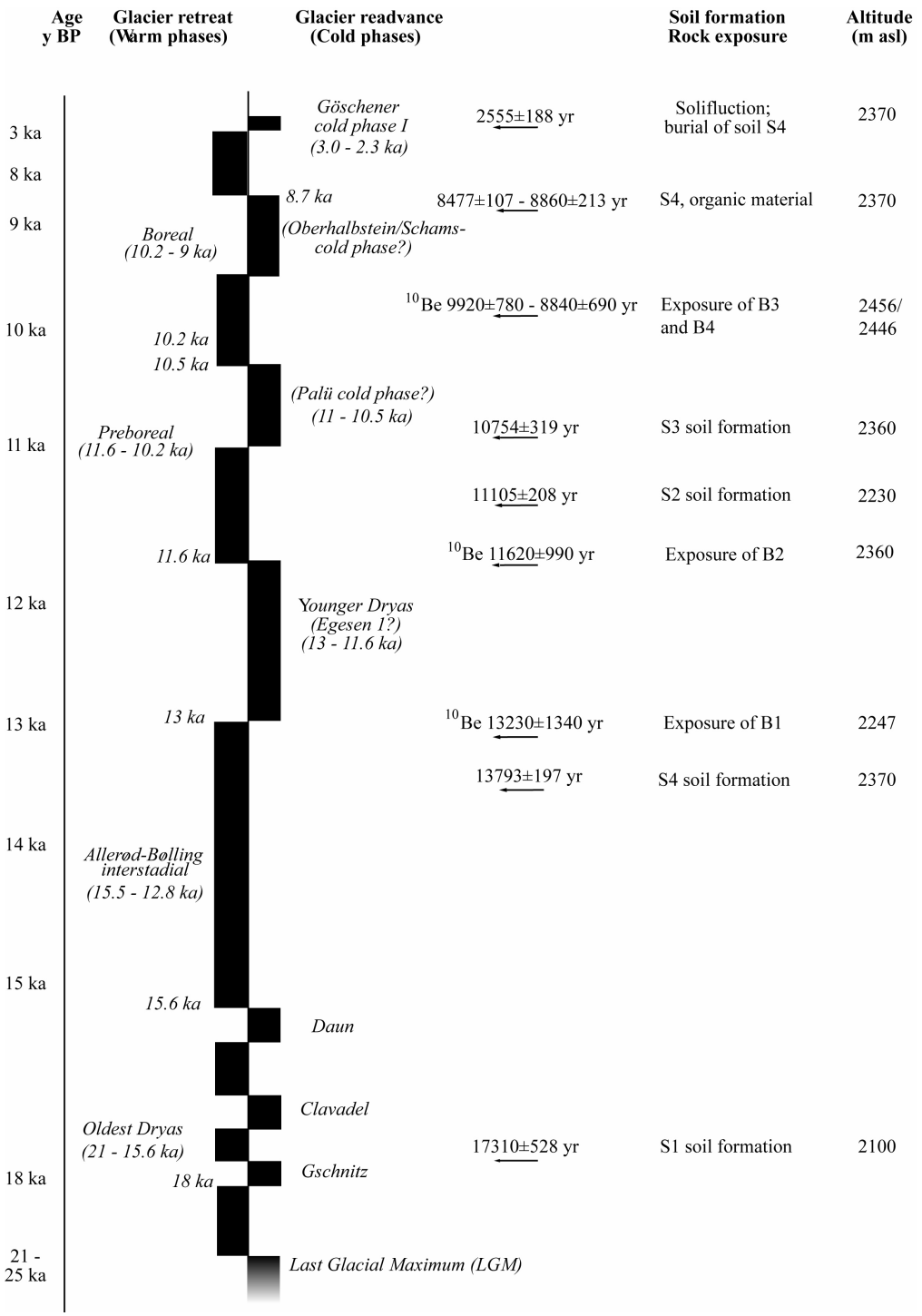

Figure 4 Ages of the investigated sites (^{14}C calibrated age and ^{10}Be) related to the chronology of the Lateglacial and Holocene glacier and climate variations (according to several authors, e.g. Maisch 1987; Maisch et al. 1999; Kerschner et al. 1999; Ivy-Ochs et al. 2004).

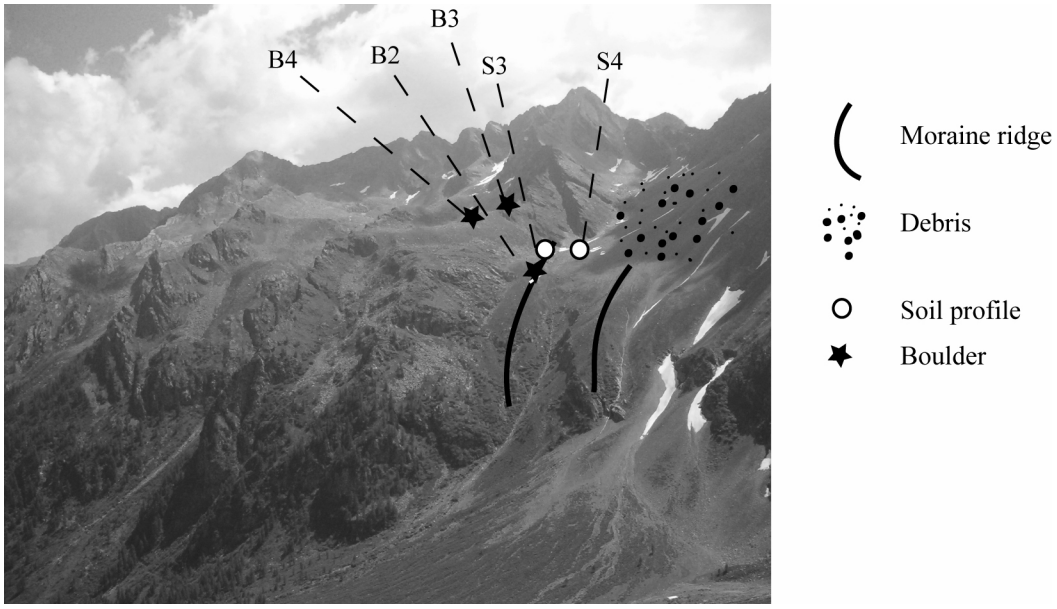

Figure 5 Location and geomorphic details in the surroundings of the profiles S3, S4 and of the boulders B2, B3, and B4

mineral phase, especially with clay minerals (Righi and Meunier 1995). Clay organic complexes, once formed, do not easily exchange the organic component with infiltrated younger humus components (Scharpenseel and Becker-Heidmann 1992). A higher ^{14}C age in the topsoil or near the surface should be the theoretical expectance since soil formation starts at the surface and proceeds with time into greater depths. Organic matter from plants and animals is incorporated into soil material and mixed with the mineral part. Because the investigated soils are podzols and consequently have a low biological activity and no earthworms, the highest ages of the stable SOM should be found in the topsoil. Such a typical trend is found in profile S1. Biological activity is low in these soils. Hence, mixing of organic material into greater depth takes a rather long time. Bioturbation is, however, not the only process of downward movement of organic matter. Due to podzolization, organic matter has been translocated into greater soil depths. In contrast to the H_2O_2-treated samples, the untreated samples show an increase of age with soil depth. This is explained by a continuous rejuvenation of SOM from the soil surface. Most of modern carbon is <100 yr old and decreases exponentially with increasing depth, leading to an increase of the percentage of old carbon present (O'Brien and Stout 1978; Mikutta et al. 2006). Hence, the ratio young SOM:old SOM should be higher in the topsoil than in the subsoil. The ratio of the H_2O_2-resistant C (old C) to total C was in the subsoil usually between 20–30% and in the topsoil in most cases <10%. On one hand, it seems that at least a part of the oldest fraction is still present in the top- and subsoil and that the treatment with hydrogen peroxide is able to detect some of the initially formed OM. On the other hand, it does not seem that in every case the oldest organic material can be found in the topsoil. This means that the top- and subsoil material has to be dated to obtain the oldest SOM fraction. ^{14}C ages prove the late Pleistocene and Holocene age of the surfaces. The ^{14}C ages of resilient SOM fit well to the ^{10}Be ages of rock boulders. ^{14}C dating of stable organic matter therefore seems to be a promising tool for dating Holocene- and late Pleistocene-aged soils. The significant linear correlation found between the ^{14}C and ^{10}Be ages and the altitude of the investigated sites enables hypotheses about the chronology of glacial and periglacial processes that occurred in the investigated area. Therefore, the combination of these 2 dating techniques helps to decipher landscape history of high Alpine regions on siliceous parent material in the late Pleistocene/Holocene.

The investigation area experienced deglaciation between 18,000 and 9000 cal BP. The ages of the soils and of the exposed boulders reflect quite clearly the movement and the timing of the glacier retreat and—in a general sense—the dynamics of Alpine landscape geomorphology. The ages of the soils and of the exposed rocks correspond quite well with the general chronology of the Lateglacial and the Holocene period, even if some aspects remain open. Deglaciation from the LGM occurred worldwide during the 3 millennia 18–15 kyr BP, documented by ice cores (e.g. Johnsen et al. 1992, 2001) and global sea-level records (e.g. Yokoyama et al. 2000). Studies from the Upper Engadine (Switzerland) indicate that retreat of the main valley glacier was substantially progressed already at 16 kyr (Studer 2005). This fits well with the ^{14}C age of stable organic matter extracted from the soil S1 having an age of around 17,000 cal BP.

The overall trend of deglaciation continued after ~15 kyr but was interrupted by extensive glacier re-advance around 16,000 to 17,000 yr ago (Gschnitz stadial; Ivy-Ochs et al. 2006b and references therein) and reflects an ELA 650–700 m below that of the Little Ice Age reference ELA (Ivy-Ochs et al. 2006b). Similarly, the age of 14,160–14,964 cal BP in the topsoil of profile S1 could point to a re-advance of local glaciers and deposition of moraine material in the Oldest Dryas. In this case, profile S1 would be polygenetic (burial of a pre-existing soil surface with the start of a new soil development). A polygenetic soil is, however, rather improbable as no signs of accumulation and burial were visible and measurable, e.g. by a distinct increase of rock fragments (material >2 mm) near the surface (see Table 3). Until the end of the Gschnitz stadial the oscillations of the glaciers occurred down to an altitude of around 1700 m asl. The period between about 15.5 and 12.8 kyr has been recognized as the Bølling-Allerød interstadial (Alley et al. 1993; Maisch et al. 1999; Schaub et al. 2008). ^{14}C dates with varve counting indicated that the Upper Engadine lakes became ice-free prior to approximately 13.5 kyr (around 16,000 cal BP) (Ohlendorf 1998). During this period of warming, Val di Rabbi also experienced a further retreat of its glaciers in a relatively short period of time compared to the overall deglaciation. After the "Younger Dryas" (about 13.0–11.6 kyr; e.g. Mangerud et al. 1974; Lundqvist 1986; Maisch et al. 1999), soils started to develop also at higher altitudes (e.g. profile S2).

The 2 boulders on the highest elevation moraine have ^{10}Be exposure ages of 8840 ± 690 and 9920 ± 780 yr. Their average age points to around 9500 yr. They may have been deposited during a re-advance phase in the Boreal (Oberhalbstein/Schams cold phase?). Periglacial activity measured probably increased around 2366–2743 cal BP (profile S4). This would fit with the "Göschener I" cold phase, which occurred between 3.0–2.3 kyr (Zoller et al. 1966) (Figure 4). Preweathered sediments containing already organic material (having an age between 8370–9073 cal BP) were deposited on top of the original soil (Figure 2, Table 5). According to previous studies (Egli et al. 2001), the formation and development of podzolization features at this altitude takes at least 1000–3000 yr. Typical podzolization features did not develop in these 2600-yr-old slope deposits. Some 2600 yr of soil evolution were obviously not a sufficiently long time for the development of podzolic characteristics.

CONCLUSIONS

We compared and combined ^{14}C ages of stable organic matter in 4 soil profiles with the ^{10}Be exposure ages of erratic boulders in order to reconstruct the timing of deglaciation at the transition of the Pleistocene/Holocene in Val di Rabbi. We obtained the following principle findings:

- The ^{14}C data of the resilient organic matter in soils fit quite well to and can be combined with the ^{10}Be age sequence obtained from boulders.

- Extraction and dating of stable organic matter from alpine soils gives a numerical value for an ice-free minimum age for deglaciation of land surfaces and the beginning of soil formation. More research is, however, needed to confirm these results.
- Dating of resilient organic matter in soils offers new perspectives in deciphering landscape history, but has to be critically evaluated and discussed.
- ^{10}Be and ^{14}C ages correlated with elevation of the investigated site and with the chronology of the Lateglacial/early Holocene re-advance and retreat phases of glaciers.
- The combination of ^{10}Be and ^{14}C dating techniques, applied in relatively small catchments in Alpine environments, despite the limited number of samples, seems to be a promising tool for a better understanding of the geomorphology and paleoclimate.
- Obtained ages reveal the chronology of the glacial and periglacial processes that occurred in Val di Rabbi between 18,000 and 9000 yr ago.

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Manuscript III

Combined use of relative and absolute dating techniques for detecting signals of Alpine landscape evolution during the late Pleistocene and early Holocene

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ABSTRACT

A combination of three relative and two absolute (numerical) dating techniques, applied on nine soil profiles in an Alpine environment located in Val di Rabbi (Trentino, Northern Italy), was used to improve the investigation methodology of Alpine sites in response to climate change and to reconstruct the chronology of late Pleistocene and early Holocene landscape evolution. The degree of podzolisation, clay mineral evolution and the element mass balances of each site were investigated. Furthermore, the stable fraction of the soil organic matter (SOM) was extracted with 10% H_2O_2 and ^{14}C-dated. The age of the organic residues was compared with the age of charcoal fragments found in one of the studied soils and with the age of rock boulders obtained by surface exposure dating (SED) with cosmogenic ^{10}Be. Numerical dating and weathering characteristics of the soils showed a fairly good agreement and enabled a relative and absolute differentiation of landscape elements. The combination of ^{14}C-dating of SOM and SED indicated that deglaciation processes in Val di Rabbi were already far advanced by around 14000 cal BP and that glacier oscillations affected the highest part of the region until about 9000 cal BP. The development of clay minerals is time-dependent and reflects weathering intensity. We found a close link between secondary clay minerals like smectite or vermiculite and soil age as obtained by the dating of the organic residues after the H_2O_2 treatment. Calculated element mass balances strongly correlated with the ages derived from ^{14}C measurements. Old soils have lost a major part of base cations (up to 75% compared to the parent material), Fe and Al, which indicates a continuous high weathering intensity. Results of the chemical and mineralogical analyses were in good agreement with numerical dating techniques, showing the dynamics of an Alpine landscape within a relatively small area. The combination of relative and absolute dating techniques is a promising tool for the reconstruction of landscape history in high-elevation Alpine areas on siliceous substrates.

1. Introduction

In the Alpine region the formation of the current landscape is mainly related to ice retreat and readvance phases at the end of the last Ice Age (between 20000 and 11500 yr ago) and throughout the entire Holocene period. Glaciers are strong erosive agents and thus play a dominant role in shaping landforms of the Alpine areas. The pioneering work of Penck and Brückner (1901/1909) on Alpine glaciations and the structures formed by glacial retreat has raised a great interest in ice decay during the Lateglacial period (e.g., Maisch, 1981, 1987; Schoeneich, 1999; Kerschner et al., 1999; Ivy-Ochs et al., 2004, 2006a,b, 2007). Many authors have described glacier fluctuations in the Alps during the Holocene (e.g., Holzhauser 1984; Hormes et al., 2001; Holzhauser et al., 2005; Joerin et al., 2006, 2008). However, only few of these studies include reliable absolute ages (Heitz et al., 1982; Maisch 1987; Schlüchter 1988; Kerschner et al., 1999; Ivy-Ochs et al., 2006a,b, 2007, 2008) because of the various limitations of the dating methods and the rareness of suitable sampling sites. The chronology of the Lateglacial is at present poorly established and is based on only a few and often questionable minimum dates (e.g., ^{14}C on basal samples of peat bogs), selected pollen profiles (Filippi et al., 2007) and the analysis of lake sediments (Larocque and Frinsinger, 2008) or morainic ridges (Baroni and Carton, 1990).

The movements of the ice resulted in the deposition of glacial till (Strahler and Strahler, 1987). When the ice retreats, the originally covered landforms and deposits become exposed to the atmosphere and weathering and soil formation can start. The process of weathering is strictly linked to pedogenesis and both are difficult to examine

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discretely (Darmody et al., 2005). The accumulation of organic material in fractures and microtopographic depressions facilitates the alteration of the bedrock and plant establishment, accelerating local weathering rates (Phillips et al., 2008). Knowledge about weathering rates and mineral transformation processes is fundamental for analysing the evolution dynamics of the corresponding ecosystem (Egli et al., 2003a). Soil surfaces are strictly bound to the environment and the climate where they have developed and reflect the impact of the soil-forming factors (Birkeland et al., 2003). For this reason, soils are essential for detecting qualitative transformations of an Alpine landscape (Egli et al., 2003a): they give the opportunity to date the retreat stages of the glaciers and to investigate the subsequent geomorphological modifications that occurred during the late Pleistocene and early Holocene. Soils that developed on glacial and periglacial substrates can be used as archives of changing weathering conditions and landscape evolution (Munroe, 2008). The presence of a great variety of microenvironments leads to a high variability in their morphology and taxonomy (Dixon and Thorn, 2005). Several methods have been developed to distinguish palaeosurfaces of different ages within soil profiles. Soil pH, translocation of organic matter, and development of typical spodic horizons all seem to attain a steady state within a few hundred to thousands of years (Egli et al., 2003b). The podzolisation process involves vertical translocation of Al and Fe by means of mobile chelate complexes. This process is linked to the duration of soil evolution and was used as a relative indicator of surface age and stability (Briggs et al., 2006). Even if these methods are not all suitable in the Alps (Fitze, 1982; Veit, 2002), they can help to provide a more detailed understanding of the glacial and periglacial processes which occurred during the late Pleistocene and early Holocene.

Dating of soil organic matter (SOM) with ^{14}C can be suitable under certain circumstances. Organic substances like aliphatic macromolecules (e.g., lipids, cutins, waxes) or aromatic substances (e.g., charcoal, lignin) can have a very long turnover time in soils especially when they are adsorbed onto mineral surfaces (Scharpenseel and Becker-Heidmann, 1992; Righi and Meunier, 1995; Favilli et al., 2008). Combining soil chemical and physical characteristics with the dating of resilient organic matter and boulders that are erratically transported by the glacier to their present positions allows for a better understanding of the natural history of the area.

The aim of this study was to use, test and compare three relative and two absolute dating techniques to establish a better methodology for the investigation of Alpine sites in response to past climatic changes. According to the obtained results we hypothesised the timing of changes in an Alpine landscape and the geomorphological history of the area. We thus applied relative dating techniques using pedogenetic and weathering parameters which are based on the premise that soil development is time-dependent (Zech et al., 2003). In addition, we used numerical methods such as surface exposure dating (SED) with ^{10}Be and dating of organic residues and charcoal fragments with ^{14}C. This work was intended to be a continuation of the methodological investigation started by Favilli et al. (2008) and was applied in the area investigated in Favilli et al. (2009). We expected to find a strong improvement in the investigation methodology by checking the reliability of ^{14}C ages with ^{10}Be exposure ages and subsequently calibrating the relative age dating of landforms in the close vicinity. The use of all these methods allows an extended interpretation, mutual control and a more accurate determination of possible sources of error.

2. Regional setting and sampling

2.1. Investigation area

The investigation area is located in Val di Rabbi, a lateral valley of Val di Sole, in the south Alpine belt in northern Italy (Fig. 1). The climate of the whole valley ranges from temperate to alpine (above the treeline). Mean annual temperature ranges from 8.2 °C (valley floor—around 800 m asl) to around 0 °C (at 2400 m asl) and mean annual precipitation from c. 800 to 1300 mm (Servizio Idrografico, 1959). Maximum precipitation occurs during the summer months. The altitudinal range of the investigation area is restricted to the alpine zone (2100–2600 m asl; Egli et al., 2008). The treeline is close to 2100–2200 m asl and forests are dominated by the conifers *Larix decidua* L. and *Picea abies* L. (Pedrotti et al., 1974). Areas above 2300 m asl are covered with rocks, boulders and short-grass meadows dominated by *Carex curvula* All. and *Nardus stricta* L. The soils and boulders investigated (Tables 1 and 2, Figs. 1 and 2) were situated between 2083 m asl and 2552 m asl, i.e., close to the treeline and in the alpine zone. The whole landscape near the investigation area has been strongly influenced by former glaciers and all the soils developed on lateral and recessional moraines consist of paragneiss. According to the geomorphological studies of Baroni and Carton (1990), Filippi et al. (2007) and Favilli et al. (2009), the surface exposure (after glacier retreat) can be dated back to about 18 000–11 000 yr BP. Large lateral moraines extend down to 1700–2000 m asl and glacial features, such as boulders and rockglaciers, can be found up to 2600 m asl. Large boulders (>2 m^3) with prominent quartz veins in flat and stable positions are present and widespread throughout this area. These boulders were chosen, where possible, near the investigated soils in order to enable a direct comparison between the ^{14}C ages (of the soils) with the ^{10}Be ages (of the boulders—see below).

The soil types present are *Entic Podzol*, *Umbric Podzol* and *Haplic Podzol* at lower altitude (2000–2200 m asl), *Protospodic Leptosol* and *Brunic Regosol* (*Cambisol*) developed at around 2300 m asl and *Cambic Umbrisol* and *Umbric Podzol* are found at the highest altitude (2500 m asl) (World Reference Base, IUSS working group, 2007). According to Soil Taxonomy (Soil Survey Staff, 2006), the soil moisture regime is udic (humid conditions, <90 days/yr with a dry soil) at all sites and the soil temperature regime is cryic (mean annual temperature <8 °C, no permafrost).

2.2. Sampling

We investigated nine soil profiles developed in the alpine belt on different morainic sediments estimated to have been deposited between the Oldest Dryas (Gschnitz/Clavadel/Daun readvance stadials; approx. 18 000 yr ago) and the Boreal chronozone (10 200–9000 yr ago; Maisch et al., 1999; Kaplan and Wolfe, 2006) (Fig. 1). The soils were investigated with respect to the degree of podzolisation, content in clay minerals and element mass balances of the upper horizons compared to the parent material. Furthermore, we compared the radiocarbon age of the resilient organic matter with that of charcoal fragments and with the ^{10}Be age sequence from 10 erratic boulders. Soil material was collected from excavated pits and undisturbed soil samples were taken, where possible, down to the BC horizon. Two to four kilograms of soil material were collected per soil horizon (Hitz et al., 2002). The soils S1, S2 and S5 developed near the treeline inside a northeasterly-exposed glacial cirque defined by Monte le Pozze e Cima Tremenesca (Fig. 1). S3 and S4 developed at 2370 and 2380 m asl respectively on a northwesterly-exposed end of Egesen/Preboreal (estimated) morainic sediment in the southern part of the same glacial cirque. S6 and S7 can be found in the northerly-exposed side of the morainic sediments on which S1, S2 and S5 developed. S8 and S9 are located in the eastern part of the transfluence pass (Passo Cercèn) at the foot of a presumed inactive rockglacier and on the ridge of a recessional moraine (estimated as end Egesen/Preboreal), respectively.

Ten large boulders with volumes >2 m^3 located on lateral moraines were sampled for surface exposure dating (see also Favilli et al., 2009). The lithology is granitic gneiss (Boulders B1–B7) and paragneiss, i.e. micaschists (Boulders/rock outcrops B8–B10). The

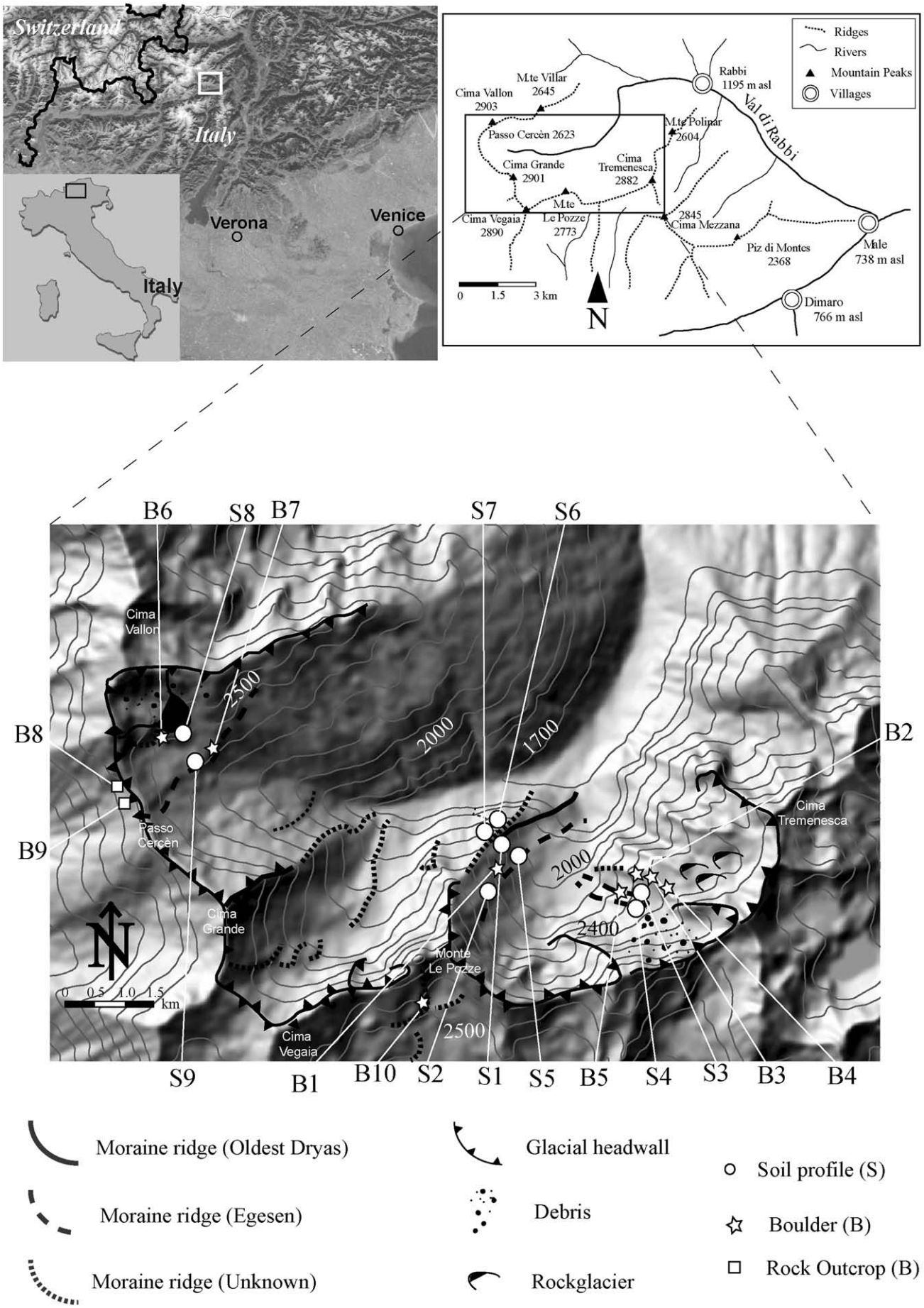

Fig. 1. Location of the investigation site.

Table 1
Characteristics of the study sites.

Soil profile	Elevation (m asl)	Aspect (°N)	Slope (%)	Parent material	Location	Estimated Lateglacial chronozone	Vegetation	Land use	WRB (IUSS Working Group, 2006)
S1	2100	60	32	Paragneiss	Lateral moraine	Oldest Dryas	*Larix decidua/Juniperus cimmunis*	Natural forest	Entic Podzol
S2	2230	70	55	Paragneiss	Lateral moraine	Egesen	*Rhododendro-vaccinietum extrasilvaticum*	Natural grassland	Haplic Podzol
S3	2380	320	5	Paragneiss	Lateral moraine	Egesen	*Festucetum*	Natural grassland	Protospodic Leptosol
S4	2370	300	10	Paragneiss	Solifluction	Boreal	*Festucetum*	Natural grassland	Brunic Regosol
S5	2083	240	32	Paragneiss	Lateral moraine	Egesen	*Larix decidua/Juniperus communis*	Natural forest	Entic Podzol
S6	2076	5	38	Paragneiss	Lateral moraine	Egesen	*Larix decidua/Juniperus communis*	Natural forest	Entic Podzol
S7	2100	3	43	Paragneiss	Lateral moraine	Egesen	*Larix decidua/Juniperus communis*	Natural forest	Umbric Podzol
S8	2552	200	33	Paragneiss	Inactive rockglacier	Boreal	*Carex curvula/Nardus stricta*	Natural grassland	Cambic Umbrisol
S9	2449	90	0	Paragneiss	Recessional moraine	Preboreal	*Carex curvula/Nardus stricta*	Natural grassland	Umbric Podzol

boulders were transported by a glacier or a rockglacier (B6) and were, since the time of the last glacial retreat, exposed to cosmic rays without being moved from their present position (Gosse et al., 1995; Table 2). For dating purposes, these boulders were chosen in a stable position in order to minimise the influence of boulder and slope instability (Table 2). As far as possible, boulders were taken in the vicinity of soil sites to enable comparison with ^{14}C data. B8 and B9 were rock outcrops and were sampled in a small cirque to identify the corresponding glacial retreat. Quartz samples were collected with a hammer and a chisel from the flat tops of the boulders (Ivy-Ochs et al., 2004). Boulder locations are shown in Fig. 1. Boulders B1 through B5 are found in the cirque defined by Monte Le Pozze and Cima Tremenesca. Boulder B1 is located on the distal side of a lateral moraine along the western side of this cirque in close proximity to soil sampling sites S1, S2 and S5. Boulder B2 is on the crest of an Egesen (estimated) lateral moraine along the south-eastern side of the same cirque. Boulders B3, B4, and B5 are located on different lateral moraines at a slightly higher elevation than B2. Boulders B6 and B7 are found in the cirque just to the east of Passo Cercen. B6 is at the foot of a rock glacier where the soil S8 is also located; B7 is on a frontal (recessional ?) moraine ridge close to soil S9, while B8 and B9 (both rock outcrops in a small cirque, west-facing) are below the former transfluence pass (Passo Cercèn). B10 is located just south of the ridge line below Monte Le Pozze, close to a lateral morainic sediment of unknown age in the south-exposed side of the investigated area (Fig. 2). According to their geomorphological position, the boulders were likely to have been deposited at different times by glaciers and can be considered representative of the chronology of deglaciation of the investigated area.

3. Materials and methods

3.1. Soil chemistry and physics

The soil samples were air-dried, large aggregates were gently crushed by hand and sieved to <2 mm. Total C and N contents of the soil were measured using a C/H/N analyser (Elementar Vario EL, Elementar Analysensysteme GmbH, Hanau, Germany) on oven-dried (105 °C) and ball-milled fine earth samples. Soil pH (in 0.01 M $CaCl_2$) was determined on air-dried samples of fine earth using a soil solution ratio of 1:2.5. After a pre-treatment with 3% H_2O_2, the particle size distribution of the soils was measured by a combined method consisting of sieving the coarser particles (2000—32 µm) and the measurement of the finer particles (<32 µm) by means of an X-ray sedimentometer (SediGraph 5100, Micromeretics, Norcross, GA, USA). The dithionite- (Fe_d, Al_d) and oxalate-extractable (Fe_o, Al_o) iron and aluminium fractions were extracted according to McKeague et al. (1971) and analysed by AAS (Atomic Absorption Spectrometry—AAnalyst 700, Perkin Elmer, USA). Total element concentrations in the soil and skeleton (material with a diameter >2 mm) (Na, Ca, Mg, K, Fe, Al, Si, Mn and Ti) were determined by energy-dispersive X-ray fluorescence spectrometry (X-LAB 2000; SPECTRO, Kleve, Germany) on samples milled to <20 µm.

3.2. Fractionation of stable organic matter

Assuming that chemical oxidation mimics natural oxidative processes, we treated the soils with 10% H_2O_2 to eliminate the more labile organic material from the more refractory organic matter (Plante et al., 2004; Eusterhues et al., 2005; Helfrich et al., 2007; Favilli et al., 2008). The stable fraction left at the end of the treatment should be part of the first organic matter formed in the sediment after glacial retreat (Favilli et al., 2009) and thus provide minimum ages for the deposition of the moraine and of deglaciation. Air-dried and sieved (<2 mm) soil was wetted for 10 min with few ml of distilled water in a 250 ml glass beaker. Afterwards, 90 ml of 10% H_2O_2 per gram of soil were added. The procedure was run at a minimum temperature of 50 °C throughout the treatment period. The beakers were closed with two layers of parafilm to avoid evaporation of the reagent. Peroxide treatments were performed for 168 h (7 days). At the end of the treatment the samples were washed three times with 40 ml of deionised water per gram of soil, freeze-dried, weighted, analysed for total C and N and ^{14}C-dated. In addition to the stable fraction, also the age of the bulk soil organic matter was dated. Site S4 has a buried soil. To derive the age of burial, the remaining roots of the sample were treated with hydrochloric acid, followed by a treatment with sodium hydroxide to remove humic acids formed during the decomposition process.

3.3. Charcoal

Charcoal fragments were separated from the soil material by hand-picking and dried at 40 °C. The individual particles were analysed microscopically and separated into coniferous and broad-leaved tree species (Schoch, 1986) with a stereomicroscope (magnification 6.4–40×, Wild M3Z Leica, Germany). The charcoal fragments from the coniferous trees were further divided at the genus level using a reflected-light microscope (objectives 5×, 10×, and 20×, Olympus BX 51, Japan). The observations were compared with a histological wood-anatomical atlas, using an identification key (Schweingruber, 1990). Charcoal identification was performed at the WSL Swiss Federal Research Institute at Birmensdorf (Switzerland).

3.4. Radiocarbon dating

The CO_2 of the combusted samples was catalytically reduced over cobalt powder at 550 °C to elemental carbon (graphite). After reduction, this mixture was pressed into a target and carbon ratios were measured by Accelerator Mass Spectrometry (AMS) using the tandem accelerator of the Institute of Particle Physics at the Swiss

Table 2
List of samples, elevation latitude and longitude of the sample sites, thickness of sample, dip (angle from horizontal) of the surface sample, amount of quartz retrieved from the sample that was used for the measurement of ^{10}Be, correction factor for topography, snow, production rate, ^{10}Be measured concentration in the sample, measurement error and ^{10}Be date.

Sample	Lab Code	Elevation (m asl)	Latitude (°N)	Longitude (°E)	Location	Sample thickness (cm)	Surface dip (°)	Quartz (g)	Shield correction	Snow cover (m)[a]	Production rate (at g^{-1} yr^{-1})	^{10}Be (at g^{-1} [1E+5])	Estimated total error[b] (%)	^{10}Be date (yr)	^{10}Be date (snow corrected) (yr)	Percentage of age increase after snow correction (%)
B1	W67	2247	46.2263	10.4597	Lateral moraine	3	30	58.5745	0.931	1.3	27.70	3.23 ± 0.21	10.2	11680 ± 1180	13240 ± 1350	11.7
B2	W70	2360	46.2253	10.4757	Lateral moraine	5	38	58.5478	0.927	0.7	29.27	3.25 ± 0.15	8.5	11110 ± 940	11890 ± 1010	6.6
B3	W72	2456	46.2253	10.4767	Lateral moraine	5	30	58.5510	0.958	0.3	32.34	3.15 ± 0.18	7.8	9780 ± 770	9940 ± 770	1.6
B4	W73	2446	46.2243	10.4777	Lateral moraine	5	16	58.5528	0.959	0.3	32.84	2.86 ± 0.19	7.8	8710 ± 680	8850 ± 690	1.6
B5	W71	2360	46.2248	10.4757	Lateral moraine	5	60	58.5589	0.797	0.7	25.16	2.31 ± 0.11	11.8	9190 ± 1090	9840 ± 1160	6.6
B6	W76	2552	46.2315	10.4367	Inactive rockglacier	4	62	60.2320	0.978	0.5	34.58	3.01 ± 0.13	9.6	8720 ± 840	8960 ± 860	2.6
B7	W77	2449	46.2302	10.4400	Frontal, recessional moraine (?)	5	0	–	–	–	–	–	–	n.d.	n.d.	n.d.
B8	W74	2597	46.2308	10.4322	Rock outcrop, near transfluence pass	5	0	60.7040	0.986	0.5	36.27	4.16 ± 0.20	9.2	11490 ± 1060	12040 ± 1110	4.6
B9	W75	2586	46.2308	10.4325	Rock outcrop, near transfluence pass	5	32	61.1020	0.956	0.5	34.91	3.84 ± 0.17	7.0	11030 ± 770	11550 ± 810	4.5
B10	W68	2453	46.2170	10.4525	Recessional moraine (?)	5	0	58.5550	0.973	0.7	32.65	4.22 ± 0.15	5.7	12950 ± 740	13850 ± 790	6.5

n.d. = not determined.
[a] Average value of snow cover during 6 months.
[b] Estimated total error including measurement error and the effects of altitude, latitude and topography/depth scaling.

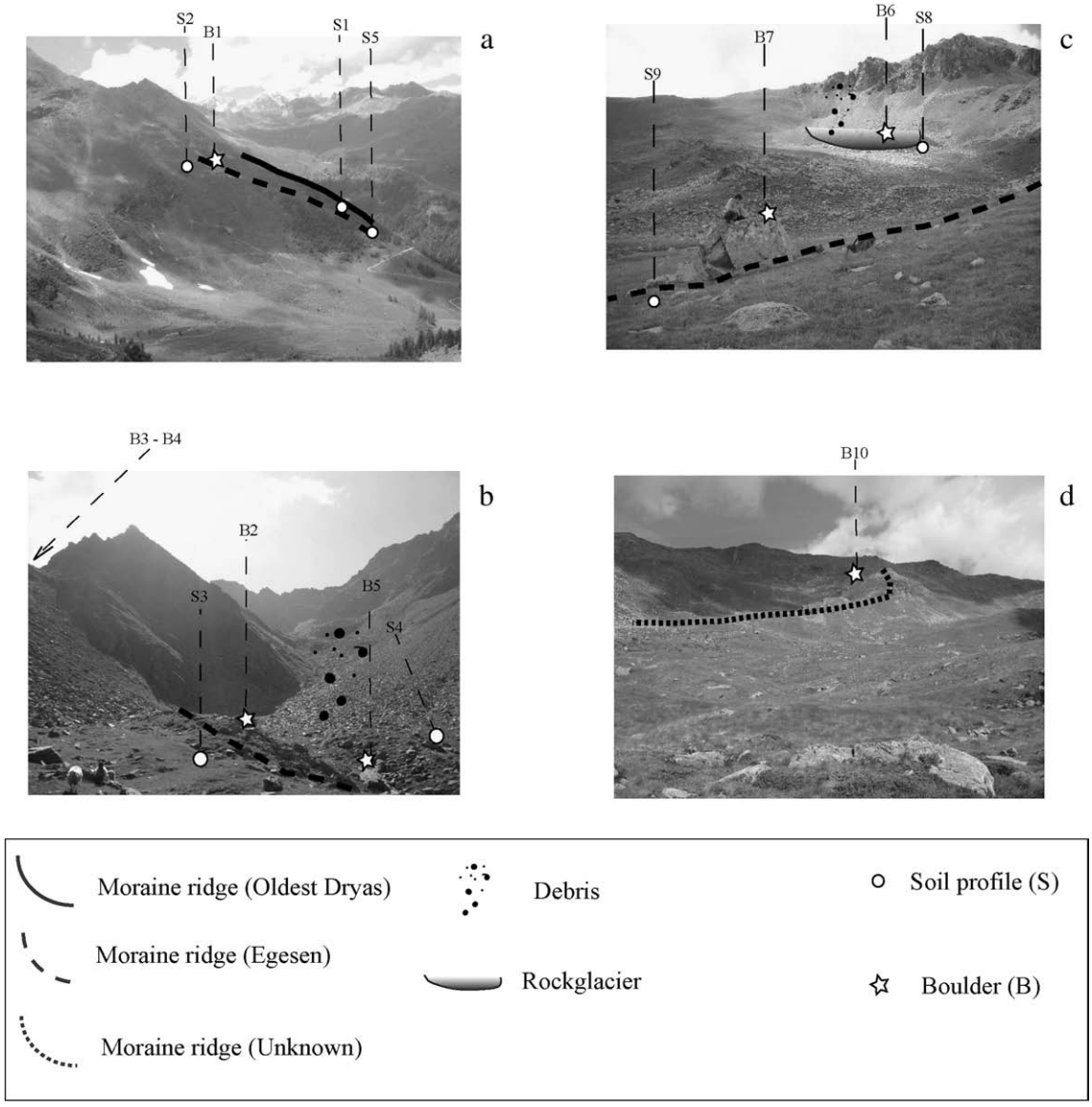

Fig. 2. a) Location of the soil profiles S1, S2 and S5 and of the boulder B1 (north–east-facing slope); b) Location of the soil profiles S3 and S4 and of the boulders B2, B3, B4 and B5 (north–west-facing slope); c) Location of the profiles S8 and S9 and of the boulder B6 and B7 (east-facing slope); d) Location of the boulder B10 (south-facing slope).

Federal Institute of Technology Zurich (ETHZ). The calendar ages were obtained using the OxCal 4.0.5 calibration program (Bronk Ramsey, 1995, 2001) based on the IntCal 04 calibration curve (Reimer et al., 2004). Calibrated ages are given in the 2 σ range (minimum and maximum value).

3.5. ^{10}Be cosmogenic nuclide dating

The rock samples were crushed, sieved and leached in order to obtain pure quartz following Kohl and Nishiizumi (1992) and Ivy-Ochs (1996). ^{9}Be solution was added to the dried quartz which was then dissolved in 40% HF. The Be was isolated using anion and cation exchange columns followed by selective pH precipitation techniques (Ivy-Ochs, 1996). The ^{10}Be/^{9}Be ratios were measured by AMS using the Tandem accelerator facility at the Swiss Federal Institute of Technology Zurich (ETHZ) using ETH AMS standard S555 (^{10}Be/^{9}Be = 95.5 10^{-12} nominal) with a ^{10}Be half-life of 1.51 Ma. The surface exposure ages listed in Table 2 were calculated using a sea-level high-latitude production rate of 5.1 ± 0.3 ^{10}Be atoms/g SiO_2/yr with a 2.2% production due to muon capture (Stone, 2000). Production-rate scaling for latitude (geographic) and altitude was based on Stone (2000) and corrected for sample thickness assuming an exponential depth profile, a rock density of 2.65 g cm^{-3} and an effective radiation attenuation length of 155 g/cm^2 (Gosse and Phillips, 2001). Topographic shielding was based on a zenith angle dependence of $(\sin\theta)^{2.3}$ (Dunne et al., 1999). Topographical shielding was calculated using a 25 m DEM and a geographical information system (ArcGIS 9.2). The production rate was corrected for mean snow cover. The snow cover was estimated according to Auer (2004) and from modern climatic data supplied by the Provincia Autonoma di Trento (Dipartimento Protezione Civile e Tutela del Territorio—Ufficio Previsioni e Organizzazione). The theoretical snow height for each sample site was estimated using a mean snow height gradient of 0.08 m/100 m altitude difference (Auer, 2004). Factors like boulder shape, wind exposition and vegetation lead to additional corrections whereas the highest reductions in snow height were caused by steeply dipping boulders. In our case the snow correction increased some of the exposure ages significantly (up to 11.7%, Table 2). A geomagnetic field correction (Pigati and Lifton, 2004) was omitted because its possible effect is small (1–2%). According to the position of the

selected boulders in the investigation area and based on results from numerous sites in the Alps, it is not likely that they were pre-exposed to cosmic rays before being deposited by the glacier (Ivy-Ochs et al., 2007).

3.6. Soil mineralogy

The clay fraction (<2 μm) was obtained from the soil after the destruction of organic matter with diluted and sodium acetate-buffered 3% H_2O_2 (pH 5), dispersion with Calgon ($Na_6O_{18}P_6$), and sedimentation in water (Carnicelli et al., 1997). Oriented specimens on glass slides were analysed by X-ray diffraction (XRD) using Cu–$K\alpha$ radiation from 2° to 15° 2θ with steps of 0.02° 2 θ at 2 s per step. The following treatments were performed: Mg saturation, ethylene glycol solvation (EG) and K saturation, followed by heating for 2 h at 335 and 550 ° C (Brown and Brindley, 1980). Clay mineral identification was performed at the Institute for Soil Study and Conservation in Florence (Italy). Digitised X-ray data were smoothed and corrected for Lorentz and polarisation factors (Moore and Reynolds, 1997). Peak separation and profile analysis were carried out by the Origin PFM™ using the Pearson VII algorithm after smoothing the diffraction patterns by a Fourier transform function. Background values were calculated by means of a non-linear function (polynomial second-order function; Lanson, 1997). The program reconstructs single peaks by fitting the envelope curve of overlapping peaks. This procedure also outputs the position and the integral intensity (area) of each single peak. On the basis of these integrals, an estimate of sheet-silicate composition was performed. The sum of the areas between 2° and 15° 2θ, which were attributed to HIV (hydroxy-interlayered vermiculites), smectite, vermiculite, mica, chlorite and kaolinite, were standardised to 100%. All treatments, including Mg saturation, ethylene glycol solvation (EG), K saturation and heating at 335 and 550 °C had to be considered for these calculations. The relative changes of the areas with respect to the treatments, enabled the above mineral phases to be distinguished. For the Mg-saturated and for the ethylene glycol solvation treatment, the area of the following peaks (d-spacings) had to be corrected by a weighting factor F: 1.6 nm with $F=0.453$, 1.4 nm with $F=0.478$, and 0.71 nm with $F=0.16$ (Niederbudde and Kussmaul, 1978; Schwertmann and Niederbudde, 1993). This procedure allowed the estimation of the relative concentrations of sheet-silicates in the clay fraction. In addition to the XRD measurement, the identification of kaolinite was confirmed by infrared (FT-IR). Spectra for FT-IR (Bruker, Tensor 27) measurements were recorded from 4000 to 250 cm^{-1} on pellets made with 1 mg of sample and 250 mg of KBr heated at 150 °C.

3.7. Calculation of weathering rates

Long-term weathering rates of soils were derived from the calculations of enrichment/depletion factors determined using immobile element content such as Ti, Zr or V. Weatherable elements must be ratioed against an inert component present in both the parent material and the soil. We used Ti as a tracer. The derivation of mass balance equations and their application to pedologic processes were discussed in detail by Brimhall and Dietrich (1987) and Chadwick et al. (1990), and revised by Egli and Fitze (2000).

Volumetric changes that occur during pedogenesis were determined by adopting the classical definition of strain, $\varepsilon_{i,w}$ (Brimhall and Dietrich, 1987):

$$\varepsilon_{i,w} = \frac{\Delta z_w}{\Delta z} - 1 \tag{1}$$

with Δz as the columnar height (m) of a representative elementary volume of protore (or unweathered parent material) p, and Δz_w is the weathered equivalent height (m) w. The calculation of the open-system mass transport function $\tau_{j,w}$ was defined by Chadwick et al. (1990):

$$\tau_{j,w} = \left(\frac{\rho_w C_{j,w}}{\rho_p C_{j,p}}\left(\varepsilon_{i,w} + 1\right)\right) - 1 \tag{2}$$

where $C_{j,p}$ (kg/t) is the concentration of element j in protolith (e.g., unweathered parent material, bedrock), $C_{j,w}$ is the concentration of element j in the weathered product (kg/t), and ρ_p and ρ_w represents the bulk density (t/m^3) of the protolith and the weathered soil, respectively.

With n soil layers, the calculation of changes in mass of element j was given by (Egli and Fitze, 2000)

$$m_{j,\mathrm{flux}(z_w)} = \sum_{a=1}^{n} C_{j,p}\rho_p\left(\frac{1}{\varepsilon_{i,w} + 1}\right)\tau_{j,w}\Delta z_w \tag{3}$$

where $\tau_{j,w}$ corresponds to the mass transport function, $\varepsilon_{i,w}$ to the strain, and Δz to the weathered equivalent of the columnar height (m) of a representative elementary volume.

Table 3
Physical characteristics of the investigated soils.

Site	Soil horizon	Depth (cm)	Munsell colour (moist)	Skeleton[a] (%)	Sand[b] (g/kg)	Silt (g/kg)	Clay (g/kg)
S1							
	AE	0–4	10 yr 3/3	5	455	280	265
	BE	4–8	5 yr 4/4	11	515	280	205
	Bs1	8–20	7.5 yr 4/4	51	575	286	139
	Bs2	20–45	10 yr 4/4	45	671	275	54
	BC	45–60	10 yr 5/4	34	n.d.	n.d.	n.d.
S2							
	AE	0–9	7.5 yr 2/1	3	397	398	205
	Bhs	9–20	7.5 yr 3/3	19	717	209	74
	Bs	20–40	7.5 yr 4/3	58	709	252	39
S3							
	AE1	0–4	10 yr 2/3	8	457	223	320
	AE2	4–12	10 yr 3/2	21	576	212	212
	Bhs	12–20	10 yr 4/2	45	638	172	190
S4							
	A	0–8	10 yr 3/2	0	352	496	152
	Bw1	8–20	10 yr 4/4	1	409	437	154
	Bw2	20–32	10 yr 4/4	32	692	258	50
	Ab	32–35	10 yr 3/3	2	309	498	193
	Bb	35–40	10 yr 4/4	49	839	136	25
S5							
	AE	0–11	10 yr 4/3	7	437	302	261
	Bs1	11–26	5 yr 4/6	16	551	344	105
	Bs2	26–50	7.5 yr 4/6	47	663	258	79
S6							
	AE	8–17	2.5 yr 5/1	54	438	417	145
	Bs1	17–38	5 yr 4/6	67	561	317	122
	Bs2	38–45	7.5 yr 4/6	68	561	317	122
	BC	45–60	10 yr 4/6	56	530	353	117
S7							
	AE	5–10	10 yr 2/1	43	498	290	212
	Bs1	11–25	10 yr 3/3	63	544	323	133
	Bs2	25–50	10 yr 3/3	44	536	331	133
	BC	50–60	10 yr 3/3	60	532	333	135
S8							
	AE	0–20	7.5 yr 3/2	37	486	374	140
	Bs	20–25	5 yr 2/4	59	599	360	41
	BC	25–48	10 yr 4/6	54	632	345	23
S9							
	AE	0–11	7.5 yr 3/2	16	381	416	203
	Bs	11–23	7.5 yr 3/3	27	497	400	103
	BC	23–40	7.5 yr 4/4	46	654	310	36

n.d. = Not determined.
[a] Skeleton = Material > 2 mm.
[b] Size fractions: sand = 2000–62 μm, silt = 62–2 μm, clay = <2 μm.

4. Results

4.1. Physical characteristics and chemical composition of the soils

The investigated soils developed on a morainic substratum over a paragneiss parent material. The proportion of rock fragments ranges from 0% up to 60% (Table 3), which is a typical value for Alpine soils (Egli et al., 2001a). All investigated soils have a loamy to loamy–sand texture. The effect of weathering is clearly visible in the decrease of the proportion of sand towards the soil surface, and in the corresponding increase in silt and clay (Table 3). Due to the siliceous parent material the soils show pronounced acidification (Table 4). Total C corresponds to organic C due to the absence of any carbonates in the soil. The podzolised soils (S1, S2, S5, S6, S7, S9) show a typical eluviation and illuviation of Fe and Al (Fig. 3). A distinct increase in dithionate and oxalate iron and aluminium was observed in all spodic horizons (Table 4). S3 was rather shallow but showed the typical characteristics of a developing podzol such as the translocation of Fe, Al and organic C into the Bhs horizon due to intense leaching conditions. Soil S4 has a polygenetic structure. At 32 cm depth, a buried soil appeared. Accordingly, a clear change in all physical and chemical characteristics was measurable due to this discontinuity (Tables 3 and 4). The soils S6 and S7 might have been influenced by slope mass movements due to the high content of skeleton (material >2 mm in diameter) towards the surface (Table 3). In these soils the degree of podzolisation (i.e., migration of Fe and Al forms in the profile) is much more pronounced at the S6 site. The soil S6 shows a clear horizon differentiation, as visible by the Munsell colour (Table 3). The amount of migrated sesquioxides is more than double in the S6 site compared to S7. The amount of organic carbon in the S7 site is constant within the profile, except in the topsoil. The topsoil of S7 exhibits almost double the amount of OM compared to the topsoil of S6 (Table 4). Soil S7 does not show a clear horizon differentiation (Table 3). A first translocation of Fe and Al forms within the soil profile was also observed in the alpine soils (S8 and S9). The degree of podzolisation was more pronounced at the site S9 than at the site S8 (Fig. 3 and Table 4).

In the investigated soils, the difference in the oxalate-extractable Al between the spodic and the albic horizon [Al_o(Bhs/Bs) − Al_o(AE/BE)] reflects the amount of pedogenic and poorly crystalline Al (Birkeland, 1999) that migrates and accumulates downward in the soil profile due to acidification of the surface and the subsequent leaching. If this difference (ΔAl_o) is plotted against the duration of soil development, using the oldest age calculated for each soil profile derived from ^{14}C data of the resilient (H_2O_2 resistant) organic matter (OM) (Table 5), then a significant correlation is observed (Fig. 4a). Chemical criteria for

Table 4
Chemical characterisation of the investigated soils.

Site	Soil horizon	pH ($CaCl_2$)	Org. C (g/kg)	Total N (g/kg)	C/N	Fe_t (g/kg)	Si_o (g/kg)	Al_o (g/kg)	Fe_o (g/kg)	Fe_d (g/kg)	Al_d (g/kg)	$Al_o + 0.5\ Fe_o$ (%)
S1												
	AE	3.7	103.7	5.7	18	27.12	0.01	1.73	5.57	15.90	2.50	0.45
	BE	3.6	61.0	2.9	21	33.63	0.01	1.91	6.06	20.50	2.80	0.49
	Bs1	4.1	39.4	1.8	22	62.44	0.00	10.27	19.62	44.10	14.70	2.01
	Bs2	4.4	17.0	0.7	24	52.50	0.00	5.84	9.37	21.40	7.30	1.05
	BC	4.5	7.5	0.6	12	49.28	0.94	4.04	1.67	6.90	5.60	0.48
S2												
	AE	3.4	184.6	28.1	7	27.69	0.00	2.78	5.67	14.53	3.94	0.56
	Bhs	3.7	63.8	11.8	5	65.10	0.07	6.31	24.90	45.33	5.96	1.88
	Bs	4.1	25.4	8.8	3	64.46	0.47	6.41	8.81	30.13	10.65	1.08
S3												
	AE1	3.4	124.9	6.8	18	17.41	0.09	2.03	2.47	8.50	2.80	0.33
	AE2	3.5	48.0	2.2	22	26.80	0.12	2.48	4.33	11.00	3.20	0.46
	Bhs	3.8	71.4	3.1	23	46.36	0.00	8.30	13.76	27.10	14.20	1.52
S4												
	A	3.8	55.3	3.8	15	59.60	0.21	3.05	7.05	21.90	5.40	0.66
	Bw1	4.0	20.7	1.5	14	69.31	0.19	2.47	9.61	30.80	5.00	0.73
	Bw2	4.1	19.5	1.3	15	60.37	0.13	1.58	4.21	20.60	3.30	0.37
	Ab	3.9	62.0	3.9	16	48.38	0.17	4.39	6.52	23.10	7.50	0.76
	Bb	4.2	9.1	0.5	18	56.16	0.09	1.57	3.70	15.30	2.70	0.34
S5												
	AE	3.5	56.9	2.7	21	35.31	0.05	2.18	7.13	21.10	3.10	0.57
	Bs1	3.8	35.3	1.7	21	69.36	0.12	6.42	20.19	50.70	9.50	1.65
	Bs2	4.3	22.8	1.1	21	56.78	0.36	6.35	10.08	24.50	8.60	1.14
S6												
	AE	3.5	76.5	4.1	19	24.64	0.022	1.49	3.88	13.54	1.82	0.34
	Bs1	4.0	45.3	1.8	25	55.7	0.089	5.60	16.46	35.81	8.21	1.38
	Bs2	4.1	47.6	1.6	30	n.d.	0.124	5.53	15.57	35.18	9.20	1.33
	BC	4.2	35.5	1.1	32	44.24	0.115	4.09	14.42	30.47	6.57	1.13
S7												
	AE	3.1	143.9	6.4	22	21.62	0.063	0.89	1.52	8.06	1.33	0.16
	Bs1	3.7	48.5	1.4	35	24.3	0.050	1.92	4.39	12.64	3.26	0.41
	Bs2	3.7	48.3	1.6	30	n.d.	0.012	1.81	3.54	10.43	2.89	0.36
	BC	3.7	48.7	1.5	32	22.7	0.036	1.90	3.64	11.12	3.23	0.37
S8												
	AE	3.8	43.0	2.3	19	31.92	0.87	4.63	6.18	22.82	7.82	0.77
	Bs	4.2	29.5	1.4	21	n.d.	2.51	6.21	6.32	19.09	8.69	0.94
	BC	4.4	8.0	0.5	16	32.97	5.75	3.30	1.97	13.92	4.40	0.43
S9												
	AE	3.2	56.4	3.8	15	18.6	0.07	3.15	4.60	12.65	3.04	0.55
	Bs	3.8	37.8	1.6	24	n.d.	0.98	7.32	10.74	31.06	8.30	1.27
	BC	4.1	17.9	0.7	26	41.02	1.42	4.08	4.01	18.64	5.91	0.61

n.d. = Not determined.
t = Total content; o = Oxalate extractable content; d = Dithionite extractable content.

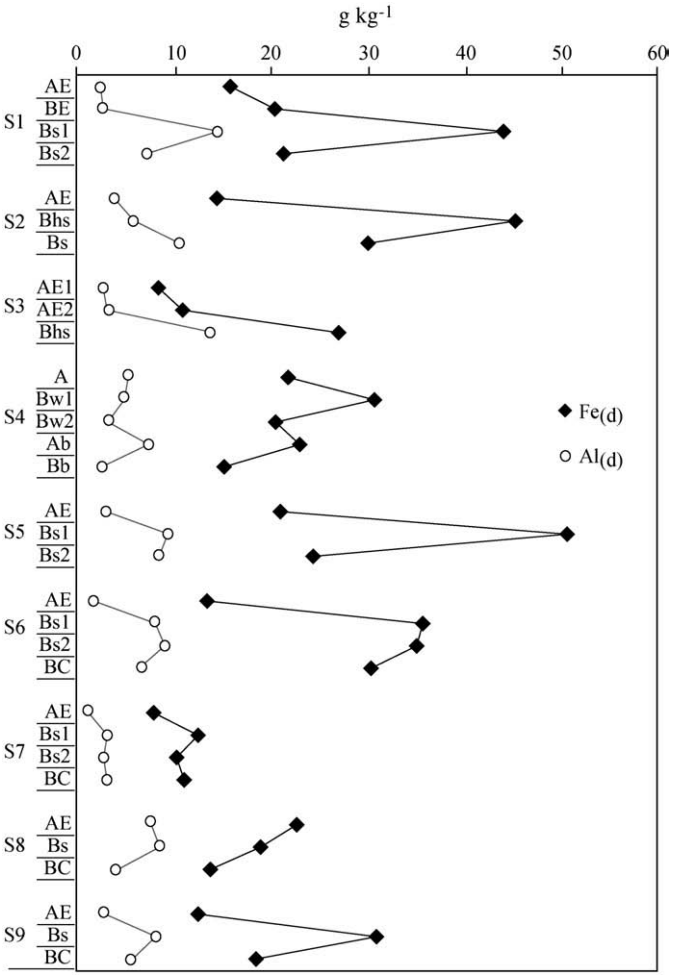

Fig. 3. Migration of Fe and Al (dithionite extraction) in the investigated soil profiles.

spodic material require that oxalate-extractable $Al_o + 0.5\ Fe_o$ is ≥0.5% and at least two times greater than in the overlying albic horizon (Soil Survey Staff, 2006; Briggs et al., 2006). In our studied soils, the average $Al_o + 0.5\ Fe_o$ value in the Bs1 (or Bhs) horizon is 1.31 (%wt) and in the AE (or BE) horizon 0.52 (%wt). The $Al_o + 0.5\ Fe_o$ values of the Bs (Bhs) horizon are 2.5–4 times greater than those of the overlying AE (BE) horizon. This criterion, too, is significantly related to the age of the resilient OM (Fig. 4b)

4.2. Radiocarbon age of soil organic matter

A decreasing age with soil depth was measured in the profiles S1, S5, S8 and S9 (Table 5). Soil profile S1, revealing an age of around 16782–17839 cal BP, may represent the first stage of deglaciation that occurred in the studied area (Fig. 5). The younger ages found in the topsoil in comparison to those in the subsoil of profiles S2, S3 and S7 are probably due to the very high C content (>11%) and either to the incapability of H_2O_2 to oxidise all young OM or to an exchange of old by younger OM. Young OM was probably able to expel older C because of the high competition for mineral-adsorption sites. The measured young age in the topsoil of S2 after the H_2O_2-treatment does not indicate the start of soil formation as the age would be much too young. The podzolic characteristics as well as the clay mineral assemblage indicate that the soil must be older (see below). The age derived from the Bs horizon would be much more plausible (10825–11386 cal BP) and may reflect a deposition of glacial sediments related to the Egesen glacial stage. The untreated soil organic matter from the subsoil of site S3 (Table 5, Bhs horizon) has a very young age. Strong leaching conditions, due to the very low pH, probably caused the downward migration of soluble young-aged organic material compounds with soil percolating water into the subsoil. The H_2O_2-treatment, performed on the sample from the Bhs horizon of S3 gave an age of 10435–11073 cal BP of the resilient OM-fraction. The polygenetic structure of the site S4 was confirmed by the ^{14}C results. Soil formation in the buried layer started around 13596–13991 cal BP and ended, due to an accumulation of eroded, unweathered material (slope deposits) between 2366 and 2743 cal BP (Table 5; Fig. 5). Plant growth, humus formation and weathering of the buried soil consequently stopped. This event was inferred from dating root residues in the Ab horizon. Preweathered and mixed sediment, already containing organic material (having an age of 8370–9073 cal BP, see Table 5 and Fig. 4), was deposited on the top of the original soil (probably by solifluction). The soil S5 has an age of around 10575–11099 cal BP. According to its age (Table 5), to its position (Figs. 1 and 2) and to the development of podzol features and clay minerals (Fig. 3; Tables 4 and 6) the sediment on which the soil profile S5 developed is of similar age as soil profile S2. The age of the soils S2, S3, S5 and S9 (see below) refer to the same period and gives a general overview of the extent of glaciation at the end of the Younger Dryas (Egesen stadial).

The ages of the resilient organic fraction in the profiles S6 and S7 were rather young and similar (between 2792–3076 cal BP in the topsoil and 5320–5584 cal BP in the subsoil). These 'young' ages compared to S1, S2 and S5 could be due to mass movements (solifluction, slope instability) until about 5000 cal BP. The real age of the sediment is likely to be much older (see the age derived from S1 and ^{10}Be dates of boulders; see below). Chemical and mineralogical data confirm the high degree of weathering these soils underwent (especially S6) during the last 5000 yr. The stability of the surface on which S6 evolved was inferred from the development of typical podzol features (Briggs et al., 2006). Soil S7, although showing the same age as S6, was much more affected by slope instabilities, as seen by the physical and chemical characteristics (Tables 3 and 4).

The stable fraction of OM in the topsoil at the site S8 (2552 m asl) has an age of 9009–9397 cal BP. The age of this soil, together with its topographical position (see Fig. 2c), gives a good insight into the timing of deglaciation in this area. Probably the material on which soil S8 developed was deposited during the 'Oberhalbstein-/Schams-Kaltphase' (around 8700–9500 cal BP; Maisch et al., 1999). Soil S9, developed at 2449 m asl, had an age in the topsoil of 10794–11600 cal BP which would fit with deposition of glacial sediments during the late Egesen glacial stage (Younger Dryas) or the early Preboreal (Ivy-Ochs et al., 2006a, 2008). In the same time range, the soils of the sites S2, S3 and S5 also started to develop (Fig. 5).

4.3. Charcoal

Dating of charcoal fragments from the horizons of one of the most well-developed profile (S5) gave increasing ^{14}C ages with soil depth with 3081–3381 cal BP in the upper horizon to 10212–10509 cal BP in the lower one (data shown in Favilli et al., 2008). The charcoal fragments could be identified as *Larix*, *Picea* and *Pinus*—the same kind of trees which currently dominate the forest. According to the plant succession model of Burga (1999), *Larix* trees are able to grow at such an altitude after about 150–300 yr of soil formation. The measured age of 10212–10509 cal BP of the charcoal and the minimum time necessary for tree growth would give a minimum age of soil formation of about 10500–10800 cal BP which corresponds very well with the measured age of the resilient organic matter fraction after the H_2O_2 extraction (in the surface horizon).

4.4. ^{10}Be exposure ages

The ^{10}Be ages of the sampled boulders range between 13850 ± 790 yr and 8850 ± 690 yr (Table 2). Boulder B10 (Fig. 2d, Table 2) was

Table 5
Measured and calibrated radiocarbon ages of untreated and H_2O_2-treated soil samples.

Site	Soil type, depth (cm)	Soil horizon	ETH numbers untreated	Uncal ^{14}C untreated	Cal ^{14}C untreated	ETH numbers H_2O_2-treated	Uncal ^{14}C H_2O_2-treated	Cal $^{14}CH_2O_2$-treated
S1	Entic Podzol							
	0–4	AE	ETH-33323	−650 ± 40	Modern	ETH-33508	12,470 ± 90	14,160–14,964
	4–8	BE	ETH-33324	−30 ± 40	Modern	ETH-33509	14,410 ± 110	16,782–17,839
	8–20	Bs1	ETH-33325	780 ± 40	666–772	ETH-33510	10,060 ± 85	11,274–11,972
	20–45	Bs2	ETH-33326	2815 ± 45	2794–3064	ETH-33511	9735 ± 75	10,786–11,270
	45–60	BC	–	–	–	–	–	–
S2	Haplic Podzol							
	0–9	AE	–	–	–	ETH-33972	2360 ± 50	2207–2699
	9–20	Bhs	–	–	–	–	–	
	20–40	Bs	–	–	–	ETH-33973	9775 ± 70	10,825–11,386
S3	Protospodic Leptosol							
	0–4	AE1	–	–	–	ETH-33976	5115 ± 55	5729–5989
	4–12	AE2	–	–	–	–	–	
	12–20	Bhs	ETH-34208	650 ± 50	546–676	ETH-33977	9425 ± 75	10,435–11,073
S4	Brunic Regosol							
	0–8	A	–	–	–	ETH-33974	7655 ± 65	8370–8585
	8–20	Bw1	–	–	–	–	–	–
	20–32	Bw2	–	–	–	ETH-35573	8025 ± 60	8647–9073
	32–35	Ab	ETH-33978	2505 ± 50	2366–2743	ETH-33975	11,920 ± 85	13,596–13,991
	35–40	Bbw	–	–	–	–	–	–
S5	Entic Podzol							
	0–11	AE	ETH-33515	85 ± 50	10–237	ETH-33512	9495 ± 75	10,575–11,099
	11–26	Bs1	ETH-33516	570 ± 50	518–654	ETH-33513	8125 ± 70	8788–9294
	26–50	Bs2	ETH-33517	1525 ± 50	1318–1525	ETH-33514	7700 ± 75	8377–8627
S6	Entic Podzol							
	8–17	AE	–	–	–	ETH-35565	2825 ± 50	2792–3076
	17–38	Bs1	–	–	–	–	–	–
	38–45	Bs2	–	–	–	ETH-35566	4235 ± 50	4583–4874
	45–60	BC	–	–	–	–	–	–
S7	Umbric Podzol							
	5–10	AE	–	–	–	ETH-35563	2880 ± 50	2870–3202
	11–25	Bs1	–	–	–	–	–	–
	25–50	Bs2	–	–	–	ETH-35564	4710 ± 50	5320–5584
	50–60	BC	–	–	–	–	–	–
S8	Cambic Umbrisol							
	0–20	AE	–	–	–	ETH-35567	8195 ± 60	9009–9397
	20–25	Bs	–	–	–	–	–	–
	25–48	BC	–	–	–	ETH-35568	6445 ± 55	7271–7433
S9	Umbric Podzol							
	0–11	AE	–	–	–	ETH-35383	9795 ± 85	10,794–11,600
	11–23	Bs	–	–	–	–	–	–
	23–40	BC	–	–	–	ETH-35384	7200 ± 70	7875–8175

Calibrated ^{14}C ages are given in the 2 σ range.
– = not determined.

deposited on the south-facing slope of the investigated area (Monte le Pozze) at the onset of the Bølling-Allerød deglaciation phase (14.7 to 12.9 ka; Alley et al., 1993). Boulder B1, located on the distal side of the postulated west-lateral Egesen moraine (2247 m asl), was deposited 13 240 ± 1350 yr ago during a glacial advance probably in the early Younger Dryas chronozone. Similarly, around 11 890 ± 990 yr ago, the site B2 at 2360 m asl was affected by the readvance of a small glacier tongue, most probably during the late Egesen stadial. The boulders sampled at 2450 m asl (B3 and B4) (Fig. 2b) have ^{10}Be exposure ages of 9940 ± 770 yr and 8850 ± 690 yr, respectively. Their average age is 9400 yr. They were probably deposited during a glacial readvance in the Boreal (Oberhalbstein-/Schams-Kaltphase: Maisch et al., 1999; Fig. 5). The boulder B5, having a ^{10}Be age of 9840 ± 1160 yr, is located near the same moraine where B3 (at 2456 m asl) is found. It has, however, probably been shifted away from the crest (Fig. 2b). The age of boulder B5 is very similar to that of B3, suggesting contemporary deposition. Based on the position of B5 (Fig. 2b) and on its smaller size (compared to the other boulders), we assume that this boulder was probably deposited together with B3 and then moved downward due to slope instability (rock fall?) (See, e.g., Ivy-Ochs et al., 2007).

In the western part of the investigated area, four boulders were sampled on both sides of a transfluence pass (Passo Cercèn—Fig. 1). The rock outcrops B8 and B9, sampled close to 2600 m asl in the west-facing slope of a former transfluence pass, give a mean age of 11 795 yr (Table 2). These rock outcrops indicate the deglaciation of a small, west-facing slope at the end of the Egesen stadial (Ivy-Ochs et al., 2006a, 2008). At the east-facing slope, the same glacial stage is represented by the soil S9 (at 2449 m asl—Fig. 2c) which has a ^{14}C age of 10 794–11 600 cal BP and started to develop after the Egesen glaciation, i.e. in the Preboreal. Boulder B6 is located close to soil S8 at the foot of a presumed inactive rock glacier (Fig. 2c). The ages of the boulder and the soil, 8960 ± 860 yr and 9009–9397 cal BP, respectively, agree well.

4.5. Clay minerals

The clay mineral assemblages for all profiles and horizons are given in Table 6. Clay minerals were identified according to the sitions of the peaks in the X-ray diffraction patterns (Fig. 6a, c). In the surface soil horizon, smectite compounds were measurable in all podzolised soils except in the top horizons of the soils developed at the highest altitude (S8 and S9) and in the topsoil of the polygenetic soil (S4). In the top horizons of soil profile S1 (Fig. 6a, Table 6) a high concentration of smectite was measured with a

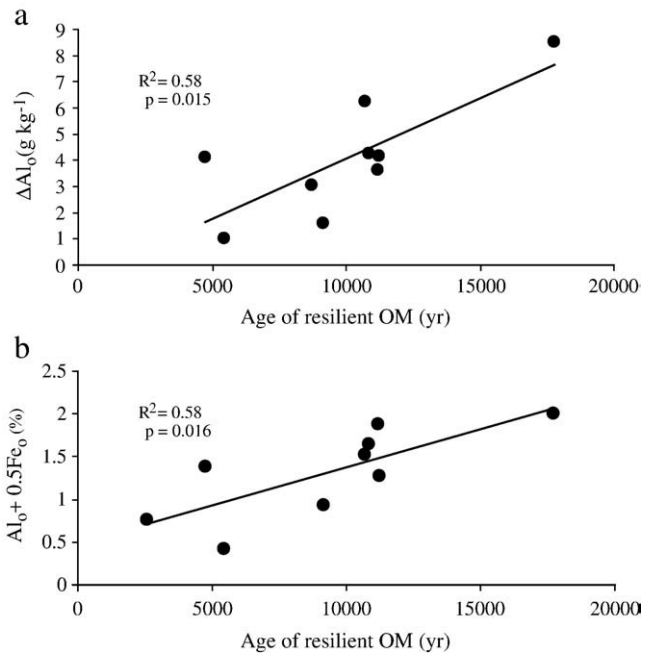

Fig. 4. a) Correlation between the content in pedogenic and poorly crystalline Al (Al_o) migrated into the Bs1 (or Bhs) horizon of the investigated soils and the age of the resilient OM. b) Correlation between the average content in ($Al_o + 0.5\ Fe_o$) in the Bs1 (or Bhs) horizon of the investigated soils and the age of the resilient OM.

concomitant decrease in chlorite (which was present especially in the subsoil). A high amount of smectite was discernible in the Bs1 horizon, together with a distinct decrease in the mica concentration. Kaolinite could be discerned by the persistence of the peak at 0.7 nm after all treatments except the one at 550 °C and by the peak at 3697 cm^{-1} by the FT-IR measurements (Fig. 6b). The same trend could be found in the S5 profile whose age is 10575–11099 cal BP (Table 5). Increasing smectite and decreasing chlorite and mica contents towards the soil surface were detectable also in the profile S2 (Table 6). The calibrated radiocarbon age of the top layer of soil profile S2 was, however, only 2207–2699 cal BP. The smectite content in the surface horizon is similar to that of profile S5 and consequently the age should be more or less similar, i.e. 11000 yr (which was the age measured in the subsoil of profile S2). A distinct erosion event is less probable, because profile S2 did not show any macromorphological signs of erosion and the whole profile is well-developed. We assume, therefore, that H_2O_2 was probably not able to remove all labile organic matter which consequently led to an unrealistically young age for the H_2O_2-resistant fraction. The high initial organic C content in the topsoil (18%) was too high for the H_2O_2 treatment. A similar effect could be measured in the soil S3 which has an organic C content in the top layer of more than 11%. The site S3 is exposed to the north, has an age of about 10435–11073 cal BP, and exhibits typical features of ongoing podzolisation (Fig. 3). This soil is highly developed and a high amount of smectite or mica/smectite was discernible in the whole profile: their increase towards the surface points to a high degree of weathering (as seen also from the organic matter and Fe–Al migration) (Figs. 3 and 4, Tables 4 and 6). The content of other clay minerals like chlorite or mica increased with increasing soil depth. The development of clay minerals in the soil profiles S2 and S3 confirmed the H_2O_2-extraction age from the subsoil. Site S4 includes a buried soil which was dated 13596–13991 cal BP. The resilient organic matter present in the top layers has an age of 8400–9000 yr. The clay mineral assemblage of the buried top layer (Ab) shows a high degree of weathering with a relatively high amount of smectite, even when chlorite is still present (Fig. 6c, Table 6). The present topsoil (A, Bw1 and Bw2 horizons) does not show clear podzolic features. No smectitic components were detected: only primary minerals or transitory weathering products such as chlorite and mica/HIV, which indicates an initial stage of weathering. Kaolinite was detected by the peak at 0.7 nm and also by FT-IR measurement (Fig. 6d, Table 6). According to the ^{14}C ages it seems that the present topsoil material was deposited around 2366–2743 cal BP (^{14}C age of root remaining in the bulk soil in the Ab horizon—Table 5). According to Egli et al. (2001b), clay mineral transformations mainly occur within the first 3000 yr of soil formation and distinct amounts of smectite can be discernible in well-developed soils after 8000 yr. The 2600 yr timespan of the present soil surface was obviously not sufficiently long for the development of major amounts of secondary minerals. In soil profile S5, having an age of 10575–11099 cal BP, a high amount of smectite was measured. Chlorite disappeared in the topsoil and interstratified mica/HIV decreased towards the surface (Table 6). The profiles S6 and S7 showed a slightly different clay evolution. In both soils, smectite was detected in all horizons, with the exception of the BC horizon of S6. In soil profile S6, the amount of smectite increased towards the surface. In S7 a more or less constant amount of smectite was measured from the Bs2 to the AE horizon, consistent with the chemical and physical data (see Tables 3 and 4). In both soils, a distinct decrease in the interstratified mica/HIV minerals was detected towards the surface (Table 6). Chlorite is present only in the subsoil. The amount of secondary minerals confirms an undisturbed evolution, at least for S6, during the last 5000 yr. The soils S8 and S9 show a decrease in the mica and HIV content from the subsoil to the topsoil. Chlorite is present in all horizons, except in the top soil. Interstratified minerals like mica/HIV could be found only in lower horizons. Vermiculite showed a decreasing tendency towards the surface. Traces of smectite are also present in the surface horizons (Table 6).

4.6. Mass balance calculations

The main geochemical data of the bulk material is given in Table 7. The composition of the investigated material reflects the acidic character of the soils. Minor differences occurred in the chemical composition of the C (BC) horizon between the sites. The Al_2O_3 content of the parent material at the sites located below the treeline (S1, S5, S6 and S7) seems to be slightly higher compared to the other sites. No significant differences are present for any other components. The variation of the state factor parent material (Jenny, 1980) seems to be negligible. Positive strains ($\varepsilon_{i,w}$) were usually measured in all profiles (Table 8). Positive values indicate dilatation due to the formation of humus or (bio)pores (Egli et al., 2001b). The open-system mass transport functions τ are listed against depth for each soil and element (Table 8). Generally negative values and thus losses of elements are observed with increasing age of the soil (Table 8). Substantial losses of Na, Ca, Mn and Mg up to 70% of the parent material were observed in the soils S1, S2, S3, S5 and S9. The polygenetic soil S4 showed losses in the top horizon (A horizon) of up to about 70% for Ca, Mn and Na and slightly lower losses in the buried top horizon (Ab).

The soils S6 and S7 that developed of a moraine of a north-facing slope and soil S8 that developed at the foot of a presumed inactive rock glacier (see Fig. 2c), did not show very intense element losses. The depletion of Al, Fe, Mg and Si was rather low compared to other soils in that region (S1, S5 and S9). Mass balance calculations and macromorphological features (high skeleton content up to the surface) indicated that these soils must have had a disturbed evolution due to solifluction or slope instabilities.

If the relative losses of base cations and Fe and Al (τ-values) are plotted against time (derived from the ^{14}C ages of the resilient organic

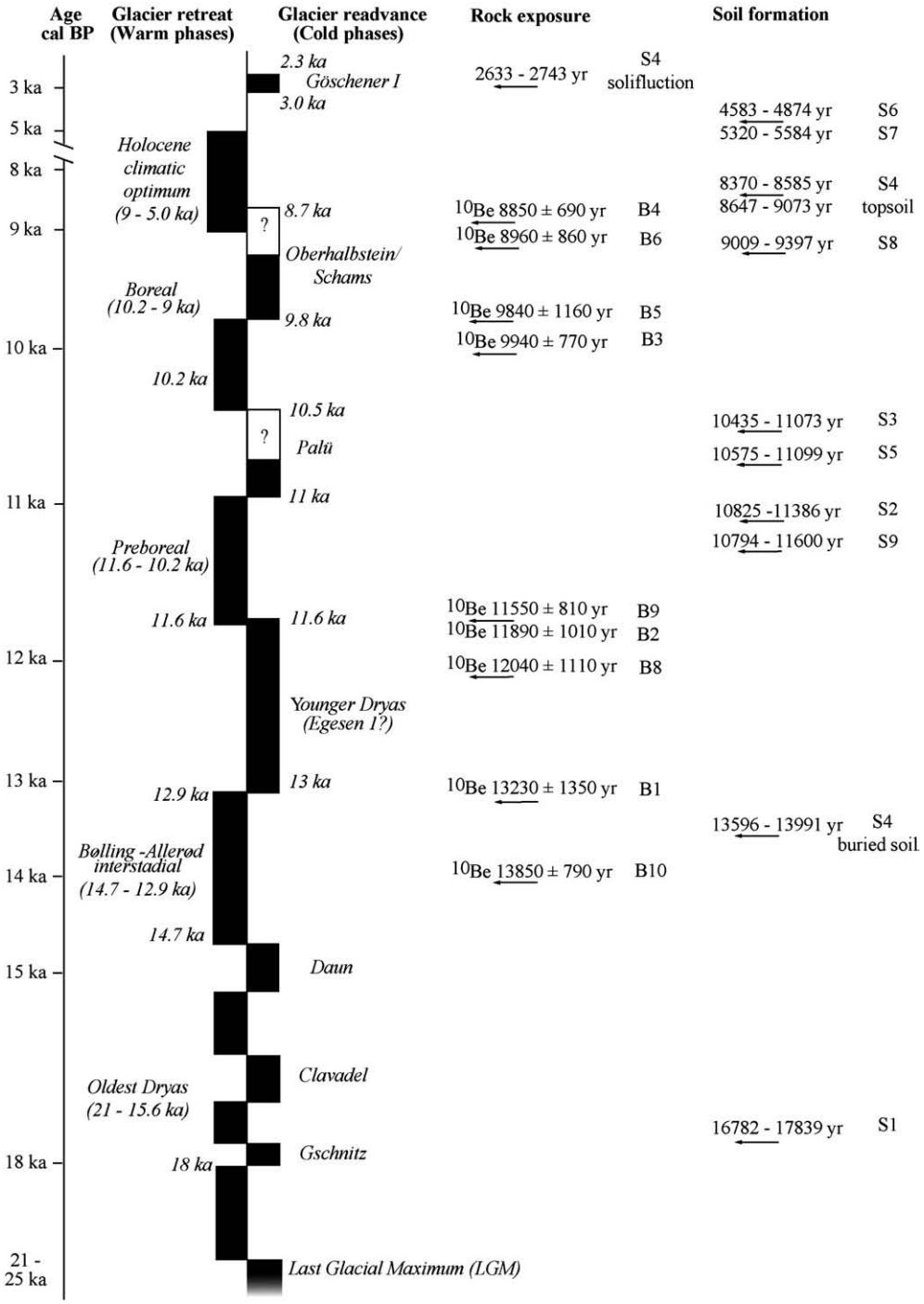

Fig. 5. Absolute ages of the investigated sites related to the chronology of the Lateglacial and Holocene glacier and climate variations (according to several authors, e.g., Maisch, 1987; Maisch et al., 1999; Kerschner et al., 1999; Ivy-Ochs et al., 2004). Question marks ("?") are used to indicate the uncertainties in the extension of the cold phases in the investigated area.

matter) then a significant correlation can be found (Fig. 7a, b). In general, the older the soil, the higher are the relative element losses.

5. Discussion

5.1. Relative dating techniques

Intense leaching conditions have favoured the downward movement of organic carbon, Fe and Al, which contribute to the development of podzol-like features. Podzolisation processes are operating in these soils, even in those that do not show a clear albic and a spodic horizon (Table 4). Eluviation and illuviation of Fe and Al forms were evident in most soils and can be seen as a function of the weathering stage and thus the time since the start of soil formation (Figs. 3 and 4). With increasing time of soil development, more Al and Fe migrate and accumulate in the spodic horizon. Therefore, the degree of podzolisation (i.e., the migration of Fe and Al in the profile) seems to be a good indicator of the soil age and of the slope processes occurring. Soil mineralogy reflects the development of the individual sites. Under undisturbed conditions for soil evolution (neither erosion nor

Table 6
Minerals in the clay fraction of the investigated soil horizons: an overview.

Site	Soil horizon	Smec[a]	Verm[a]	Mica/ smec	mica/ HIV	HIV[a]	Chlorite	Mica	Kaolinite
S1	AE	++	+	+	+	(+)	−	++	+
	BE	+	+	++	−	+	−	++	+
	Bs1	+	+	+	+	+	+	++	+
	Bs2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	BC	−	+	−	++	(+)	+	++	(+)
S2	AE	+	++	++	−	+	−	+	+
	Bhs	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Bs	−	+	−	++	+	(+)	+	+
S3	AE1	++	+	++	++	+	−	+	+
	AE2	+	++	−	−	−	−	++	+
	Bhs	+	−	++	+	(+)	+	++	+
S4	A	−	+	−	++	−	+	++	+
	Bw1	−	+	−	−	−	+	++	++
	Bw2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Ab	++	++	−	−	−	+	++	+
	Bb	−	+	−	−	+	+	++	++
S5	AE	+	(+)	++	+	+	−	++	+
	Bs1	++	+	+	+	+	+	++	+
	Bs2	+	+	++	++	−	+	++	+
S6	AE	++	(+)	++	−	+	(+)	++	+
	Bs1	+	+	++	+	(+)	+	++	+
	Bs2	+	+	++	+	+	+	++	+
	BC	−	++	−	+	+	+	+	+
S7	AE	++	(+)	++	+	+	−	++	+
	Bs1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Bs2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	BC	+	+	+	++	+	−	++	+
S8	AE	(+)	++	−	−	++	+	+	+
	Bs	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	BC	−	++	−	+	(+)	+	++	+
S9	AE	(+)	++	−	−	−	−	++	+
	Bs	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	BC	−	+	−	++	+	+	++	+

n.d. = not determined.
(+) = traces (0–5%).
+ = present in significant amount (5–20%).
++ = present in high amount (>20%).
− = not present.
[a] Smec = smectite; Verm = vermiculite; HIV = hydroxy-interlayered vermiculite.

accumulation) and no lateral water fluxes or reduced water percolation, smectites are usually the end-product of weathering in Alpine soils (Egli et al., 2003b). Usually, the longer a soil has been forming, the higher the content of smectite in the topsoil. This relation is, however, not linear. Within a soil profile, an increase of smectite towards the surface should be expected (most intense weathering conditions are near the surface). The presence of smectite in soils is due to strong leaching and weathering conditions (Carnicelli et al., 1997; Mirabella and Sartori, 1998; Egli et al., 2003b). According to Egli et al. (2001b), distinct amounts of smectites can be found in well-developed soils (Fig. 6a). Smectite and regularly interstratified dioctahedral mica/smectite could be identified generally in the most-weathered horizons (e.g., Egli et al., 2001b, 2003a). With the exception of the present top layer of the polygenetic soil (S4) and of the soils developed at the highest altitude (S8 and S9), a significant amount of smectites was measured in the surface horizons (Table 6). The formation of smectite can be traced back to the transformation of chlorite and mica through transitional steps such as hydroxy-interlayered vermiculite (or smectite), irregularly interstratified mica-vermiculite or mica-smectite (Righi et al., 1999; Egli et al., 2003b). On stable surfaces, the amount of secondary minerals in the most-weathered horizon can be used as an age indicator to relatively differentiate soil surfaces. The accumulated material on the top of the present soil at S4 (A, Bw1 and Bw2 horizons) showed no major clay mineral transformations. This agrees well with the ^{14}C age (2366–2743 cal BP) derived from the (untreated) roots remaining in the buried horizon (Ab) which gives an approximate date of the burial event. Chemical and mineralogical data of the soil profile S7 suggest that this soil was affected by greater disturbances compared to S6 during the 5000 yr of its evolution (Tables 3–5).

Mass balance calculation indicated that extensive mineral weathering resulted in significant losses of Si, major base cations, Al and Fe. These mass balances could be related to the degree of weathering and time of exposure of the sediments on which the soils developed. The rates for soils formed on transported material such as glacial till range from about 10^{-2} to 10^{1} mm/yr (Pillans, 1997). According to these values, the investigated soils would have developed 50 cm over approximately 5000 yr. This would fit very well with the obtained ages from S6 and S7 (Table 5). In addition, we must consider that the earliest stages of soil development are faster than the average rates estimated for longer time periods. Weathering and the rate of soil development over time often show a non-linear or even logistic trend (Egli et al., 2001a; Phillips et al., 2008). The most-weathered soils (S1, S2, S3 and S5), which developed within a glacial cirque, are podzolised and have a high radiocarbon age and high element losses. Soil S8 showed minor losses in base cations as expected for a 9000 year-old soil; here, a small enrichment in the Si content and no losses in Fe were measurable compared to the parent material (Table 8). This might have been caused by the deposition of material coming from a mountain ridge (rock fall?). The high amount of skeleton in the topsoil (Table 3) indicates a similar process. The high increase in the clay content in the topsoil of S8 underlines the weathering intensity under which this soil developed. Soil S9 showed relatively high cation losses compared to other soils of similar age (e.g., S2). Chemical weathering, therefore, supports the findings obtained from the physical characteristics of the soils and from numerical dating.

5.2. Absolute dating techniques

The ^{14}C ages of the soils and the ^{10}Be ages of the exposed boulders give good indications of the evolution and timing of glacial retreat in Val di Rabbi and—in a general sense—of the dynamics of Alpine landscape formation. Within a soil profile, the age of SOM varies strongly (Table 5). According to Favilli et al. (2008, 2009), the H_2O_2 treatment seems to enable the dating of undisturbed late Pleistocene/Holocene-aged soils. H_2O_2 is a strong reagent which oxidises the largest part of the labile organic matter in soils (see Favilli et al., 2008). The oldest age of the H_2O_2-treated samples was usually measured in the E or B horizon (Bs or Bhs) and gives an indication of the timing of the start of soil formation. Soil development in alpine settings began after the deposition and exposure of the sediments left by the retreating glaciers (Birkeland et al., 1987). Soil charcoal dating was added as further temporal evidence for soil pedogenesis (Carcaillet, 2000). The oldest charcoal fragments were found in the deepest soil horizon, in accordance with the assumption of the stratification of wood charcoal in soil (Carcaillet, 2001). The ^{14}C ages of the H_2O_2-treated samples and the charcoal ages of profile S5 agree well and demonstrate that the oldest charcoal fragments can also give indications about start of soil formation. After about 150–300 yr of soil formation, *Larix* trees (identified charcoal piece) are able to grow at such an altitude according to the plant succession model of Burga (1999). The measured age of 10353 cal BP of the charcoal and the minimum time necessary for tree growth would give a minimum age of soil formation of about 10600 cal BP which corresponds well with the measured age of the resistant organic matter fraction in the surface horizon after the H_2O_2 extraction (10575–11099 cal BP).

The age sequences obtained from ^{14}C and ^{10}Be data allow us to infer the timing of glacier oscillations during the Lateglacial and early Holocene in the investigated area as portrayed in Fig. 5. Based on the boulder exposure dates, the investigation area was deglaciated by the beginning of the Bølling-Allerød interstadial (around 14.7–12.9 ka; Alley et al., 1993; Maisch et al., 1999; Schaub et al., 2008). Subsequent glacial readvances during the Younger Dryas (Egesen stadial) and

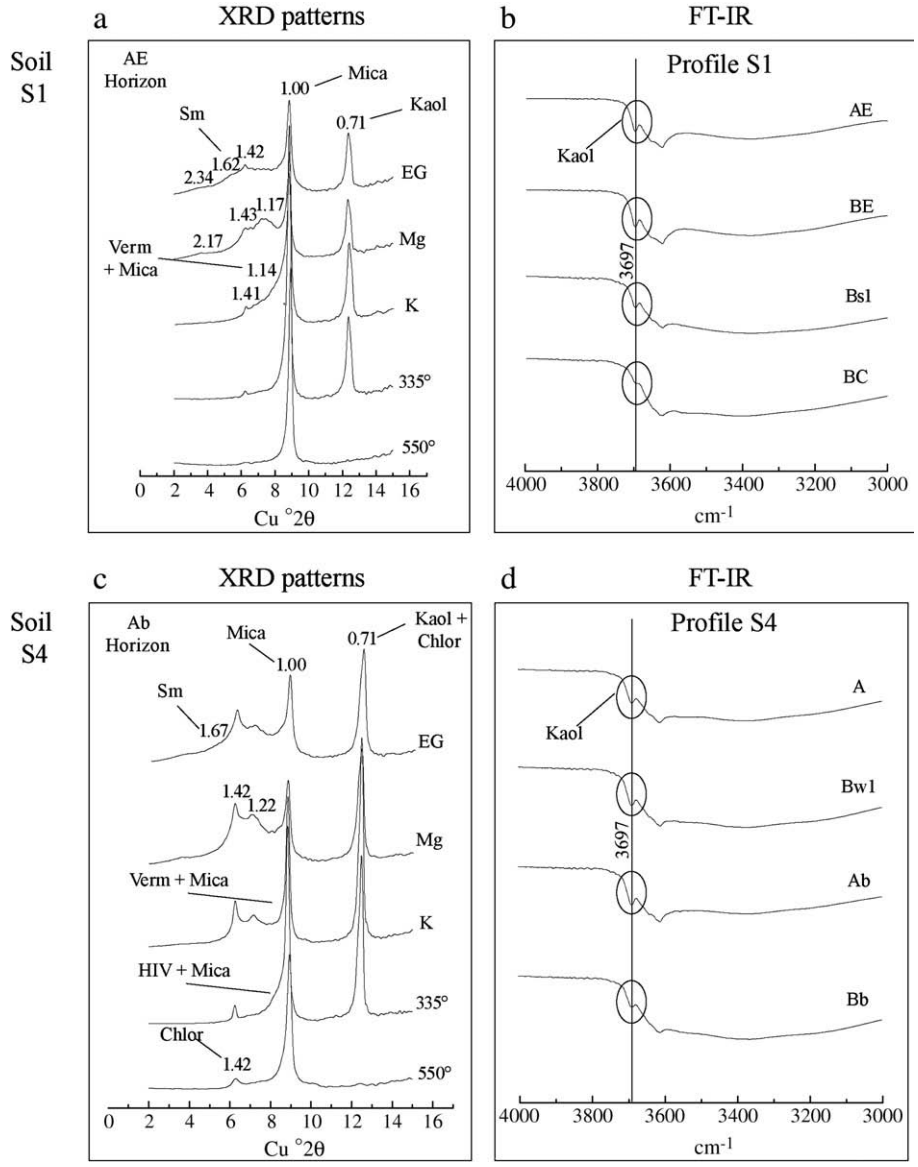

Fig. 6. X-ray patterns (a and c) of soil clays (<2 μm) and FT-IR spectra (b and d) of selected soil horizons. The XRD-curves are smoothed and corrected for Lorentz and polarization factors. *d*-spacings are given in nm. Mg = Mg saturation; EG = ethylene glycol solvation; K = K saturation and corresponding heating treatments. Sm = Smectite; Verm = Vermiculite; HIV = Hydroxy-interlayered vermiculite; Chlor = Chlorite; Kaol = Kaolinite.

possibly as late as the Boreal (9.0–10.2 ka; Maisch et al., 1999) are inferred from our ^{10}Be data (Fig. 5).

Organic material from soil S1, having an age of 16 782–17 839 cal BP, may indicate the first stages of deglaciation of the area (Figs. 1 and 5). The three applied relative dating techniques (element losses, clay mineral investigation, eluviation and illuviation of Al and Fe in the soil profile) support the hypothesis that the surface of S1 is the oldest one. Soil formation probably began after the down-wasting of Gschnitz or Daun stadial glaciers (Ivy-Ochs et al., 2006b, 2008 and references therein). Studies from Upper Engadine (Switzerland) confirm that the retreat of the main valley glacier had progressed significantly by 16 000 cal BP (Studer, 2005). Radiocarbon data indicate that the lower parts of the main valleys, e.g. the Inn valley (Van Husen, 2000), were already ice-free by 19.0 to 18.0 ka (Ivy-Ochs et al., 2006a,b, 2008). This fits well with the radiocarbon age of the stable organic matter extracted from the soil S1.

During the Bølling-Allerød interstadial, the Val di Rabbi experienced further retreat of its glaciers in a relatively short period of time. Our data show that during the Bølling-Allerød phase deglaciation had already progressed to 2100 and 2400 m asl. The age of boulder B10 (13 850 ± 790 yr) demonstrates that along the south-facing slope of Monte Le Pozze (see Figs. 1 and 2d) deglaciation occurred earlier at higher altitudes (2453 m asl). Based on the data from site S4, the north-facing side of the investigated area was deglaciated up to 2370 m asl.

The Egesen stadial (Younger Dryas) (Maisch et al., 1999; Ivy-Ochs et al., 2006a, 2008) is represented by the deposition of the boulders B1 and B2 on the lateral moraines (at around 2300 m asl on the north-facing side) and its end by the exposure of the rock outcrops B8 and B9 (at 2600 m asl on the west-facing slope) (Tables 2 and 5, Figs. 2c and 5). Subsequent soil formation (sites S9, S2, S3 and S5) could start about 11 ka BP. The age of the boulders B1, 8 and 9 (12–13 ka) is bound to glacial advance phases during the Younger Dryas. Soil formation started after the retreat of the glaciers (in the Preboreal) or the deposition of moraines (about 11 ka) and, consequently, with a certain time-lag (about 0.5–1 ka) compared to the boulders.

The cosmogenic ^{10}Be age of around 13.5–14 ka (B1) does not agree well with the beginning of the Younger Dryas (Table 2). We note that the age of this boulder increased significantly due to our correction for snow cover (more than 11%). Snow depth during the Lateglacial and

Table 7
Geochemical characteristics (total analysis of the bulk material including soil skeleton (>2 mm up to 200 mm) and fine earth (<2 mm)) of the investigated soils.

Site and soil horizon	Depth (cm)	Org. matter (%)[a]	CaO (%)	MgO (%)	K_2O (%)	Na_2O (%)	Al_2O_3 (%)	Fe_2O_3 (%)	SiO_2 (%)	MnO (%)	TiO_2
S1											
AE	0–4	17.63	0.53	0.89	3.10	1.33	14.26	3.73	51.5	0.06	0.97
BE	4–8	9.23	0.43	0.93	3.40	1.35	15.74	4.77	57.2	0.07	1.03
Bs1	8–20	3.27	0.48	1.57	3.25	1.49	15.26	7.65	52.2	0.08	0.84
Bs2	20–45	1.59	0.73	1.69	3.00	1.62	14.95	6.54	59.3	0.07	0.78
BC	45–60	0.85	0.47	2.18	3.78	1.50	16.40	6.35	58.3	0.07	0.84
S2											
AE	0–9	31.75	0.64	0.53	1.90	1.18	8.84	3.82	37.4	0.02	0.75
Bhs	9–20	8.84	0.78	1.23	2.66	1.36	12.84	9.03	44.3	0.05	0.99
Bs	20–40	1.85	1.40	2.12	2.78	1.84	14.46	8.03	57.5	0.08	0.81
S3											
AE1	0–4	19.54	0.34	0.53	2.70	1.40	11.27	2.29	48.5	0.03	0.70
AE2	4–12	6.43	0.51	0.78	3.36	1.52	13.91	3.52	60.3	0.06	0.78
Bhs	12–20	6.67	0.52	0.97	2.93	1.41	12.67	5.28	52.4	0.06	0.63
S4											
A	0–8	9.41	0.64	2.54	3.84	1.35	17.25	8.68	47.6	0.04	0.87
Bw1	8–20	3.53	0.68	2.85	4.13	1.18	18.39	10.16	49.5	0.04	0.90
Bw2	20–32	2.26	1.16	2.44	3.36	1.81	16.27	8.18	57.8	0.07	0.87
Ab	32–35	10.54	1.49	2.24	2.69	2.11	13.95	6.88	67.8	0.08	0.75
Bb	35–40	1.55	1.65	2.10	2.10	2.35	13.84	6.62	64.6	0.10	0.74
S5											
AE	0–11	9.01	0.38	0.91	3.32	1.28	15.92	5.11	54.4	0.06	1.02
Bs1	11–26	5.06	0.38	1.27	3.13	1.57	15.25	9.41	51.6	0.08	0.91
Bs2	26–50	2.05	0.53	1.56	3.37	1.42	15.72	6.86	58.2	0.07	0.79
S6											
AE	8–17	3.85	1.63	2.35	2.87	2.54	14.79	4.34	65.3	0.04	0.96
Bs1	17–38	1.69	1.06	3.24	3.44	2.00	15.32	6.60	63.4	0.06	0.89
BC	45–60	1.68	1.11	2.03	3.32	1.95	14.30	5.26	68.6	0.05	0.85
S7											
AE	5–10	8.64	0.61	2.43	4.27	1.70	16.30	4.26	59.5	0.05	0.90
Bs1	11–25	2.09	0.74	2.70	3.90	2.03	15.50	3.94	67.7	0.06	0.88
BC	50–60	2.15	0.51	2.22	3.97	1.79	15.28	3.80	66.6	0.06	0.85
S8											
AE	0–20	2.81	0.97	1.03	3.21	2.71	13.49	3.91	68.9	0.07	0.40
BC	25–48	0.43	1.50	1.58	3.41	2.55	13.87	4.14	72.0	0.09	0.43
S9											
AE	0–11	4.98	0.49	1.06	2.77	1.75	14.00	2.93	61.9	0.03	0.78
BC	23–40	1.10	1.99	3.09	2.86	2.27	14.26	5.67	65.6	0.10	0.62

[a] Organic matter = org. C (of the fine earth and skeleton) * 1.72.

Holocene is difficult to gauge (Kelly et al., 2004). Therefore, the boulder may have been deposited early on during the Egesen stadial or it may have been deposited during the Daun stadial (Maisch et al., 1999). After the Egesen stadial (Younger Dryas) and the deposition of glacial sediment, the soil profiles S2, S3 and S5 started to develop. Near the transfluence pass (Passo Cercèn), new sediment was deposited at an altitude of 2450 m asl (soil profile S9—Figs. 1 and 2c). The geographical extension of two small readvance phases in the Holocene (Palü and Oberhalbstein/Schams) is not clearly detectable in the investigated area. The ages of the soils S3 and S5 fit with the presumed timespan of the Palü cold phases in the Preboreal chronozone (Zoller et al., 1998; Fig. 5). The soil S8 (at an altitude of 2552 m asl) started its evolution most probably at the end of the Oberhalbstein/Schams cold phase or the beginning of the Holocene climatic optimum (between the Boreal and the Older Atlanticum chronozones; Maisch et al., 1999). From this we can derive that the readvance of the glaciers during the Palü and the Oberhalbstein/Schams cold phases did not reach the extent of the Egesen stadial. The soil material of site S4 started its weathering during the climatic optimum. This material originated from a surface (north-facing) above the actual site S4 and indicates that the area was completely deglaciated and soils were developing. The soil profiles S8 and S9 reflect the timing of complete deglaciation of the site very well (Figs. 1 and 2c, Table 1). The exposure age of B6 (8960 ± 860 yr) and the ^{14}C age for S8 (9009–9397 cal BP) are both around 9000 yr (Fig. 5; Tables 2 and 5), which again suggests there is good agreement between the ^{14}C of resilient OM and ^{10}Be ages (see Favilli et al., 2009). The average age of the boulders sampled on the moraine at 2450 m asl (B3 and B4) is around 9400 yr, which is in accordance with a possible readvance phase during the Boreal (Oberhalbstein/Schams cold phase; Maisch et al., 1999) (Figs. 2b and 5). At the onset of the Holocene either the investigated area was already completely deglaciated or those two readvance phases affected only the sites above the soil S4 at 2400 m asl (Fig. 5). The chemical evolution of the soil profile S3 confirms that this soil has had an undisturbed development, at 2380 m asl, during the last 10 000 yr—a timespan which leads to well-developed podzols (e.g., Barett and Schaetzl, 1992; Lundström et al., 2000). This is supported by the clay mineralogy and mass balance calculations and underlines once more that the cold phases of the Holocene period affected only the sites above 2400–2500 m asl.

The H_2O_2 oxidation process left behind intrinsically resistant organic matter (Theng et al., 1992; Cuypers et al., 2002), supporting the estimated Holocene and late Pleistocene age of the surfaces. The H_2O_2 treatment allowed the detection of part of the first organic matter formed after the moraine deposition (Favilli et al., 2008). Soil OM is composed of fractions differing in structure, genesis and age, and is exposed to various diagenetic processes. In the surface horizons of the investigated Alpine soils, 3–15% of SOM must be attributed to a very old OM fraction isolated after the H_2O_2 treatment (Favilli et al., 2008). The age of this fraction decreases with soil depth, while its proportion increases—which would fit with the findings of O'Brien and Stout (1978). The treatment with hydrogen peroxide identifies some of the initially-formed OM which is still present in the top- and subsoil. In contrast to the treated samples, the untreated samples (S1 and S5) showed an increase of age with soil depth. This was explained

Table 8
Strain coefficient ($\varepsilon_{i,w}$) and open-system mass transport function (τ) for each element investigated with respect to the sites and soil depth.

Site	Horizons	Depth (cm)	$\varepsilon_{i,w}$	τ							
				Si	Al	Fe	Mn	Mg	Ca	Na	K
S1											
	AE	0–4	0.36	−0.24	−0.25	−0.49	−0.28	−0.65	−0.03	−0.23	−0.29
	BE	4–8	0.27	−0.20	−0.21	−0.38	−0.25	−0.65	−0.26	−0.26	−0.26
	Bs1	8–20	0.90	−0.11	−0.07	0.20	0.16	−0.28	0.02	−0.01	−0.14
	Bs2	20–45	0.31	0.10	−0.02	0.11	0.14	−0.16	0.68	0.17	−0.14
	BC	45–60	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S2											
	AE	0–9	0.66	−0.29	−0.33	−0.48	−0.71	−0.73	−0.50	−0.30	−0.25
	Bhs	9–20	0.15	−0.36	−0.27	−0.07	−0.47	−0.52	−0.54	−0.39	−0.21
	Bs	20–40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S3											
	AE1	0–4	0.24	−0.17	−0.20	−0.61	−0.54	−0.51	−0.41	−0.10	−0.17
	AE2	4–12	0.06	−0.07	−0.11	−0.46	−0.17	−0.35	−0.21	−0.13	−0.08
	Bhs	12–20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S4											
	A	0–8	0.26	−0.37	0.07	0.13	−0.64	0.04	−0.67	−0.51	0.57
	Bw1	8–20	0.20	−0.37	0.09	0.26	−0.63	0.11	−0.66	−0.59	0.62
	Bw2	20–32	0.49	−0.24	0.00	0.06	−0.36	−0.01	−0.40	−0.34	0.37
	Ab	32–35	0.63	0.03	−0.01	0.02	−0.19	0.05	−0.11	−0.12	0.26
	Bb	35–40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S5											
	AE	0–11	0.29	−0.27	−0.21	−0.42	−0.39	−0.54	−0.44	−0.30	−0.23
	Bs1	11–26	0.29	−0.23	−0.16	0.19	0.02	−0.29	−0.37	−0.04	−0.19
	Bs2	26–50	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S6											
	AE	8–17	0.21	−0.16	−0.09	−0.27	−0.18	0.02	0.29	0.15	−0.24
	Bs1	17–38	−0.12	−0.13	0.01	0.19	0.13	0.51	−0.10	−0.03	−0.02
	BC	45–60	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S7											
	AE	5–10	0.70	−0.15	0.01	0.06	−0.19	0.04	0.14	−0.10	0.02
	Bs1	11–25	0.51	−0.02	−0.02	0.00	−0.04	0.17	0.39	0.09	−0.06
	BC	50–60	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S8											
	AE	0–20	0.73	0.01	0.03	0.00	−0.19	−0.31	−0.32	0.12	−0.01
	BC	25–48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S9											
	AE	0–11	1.21	−0.25	−0.22	−0.59	−0.77	−0.73	−0.80	−0.39	−0.23
	BC	23–40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

by a continuous rejuvenation of SOM from the soil surface. Most modern carbon is less than 100 yr old and decreases exponentially with increasing depth leading to a relative increase of the percentage of old carbon present (O'Brien and Stout, 1978; Mikutta et al., 2006). As soil and humus formation starts at the surface and penetrates over time to greater depths, the trend of decreasing ages (resilient OM) with increasing depth seems to be logical. The untreated SOM fraction generally shows a downward movement in the profile. SOM fractions having a rather young age can be found to a considerable depth. These fractions represent the mobile part whereas the H_2O_2-resistant fraction represents the strongly bound and immobile part.

Soil profiles S6 and S7 were ^{14}C-dated to about 5000 cal BP. This age does not indicate a readvance of the glacier tongue. These sites have most probably been affected by mass movements along the slope (slope instability or solifluction). The slope instability rejuvenated the age of these soils. Both soils were subjected to an intense soil development after the stabilisation of the slope. An intense soil development is clearly visible in soil S6 and is consistent with chemical and mineralogical data. Soil S7 has the same age as S6 but its chemical and mineralogical data show a quasi-constant value along the profile. Soil S7 does not exhibit a clear horizon differentiation and it seems to be composed of mixed weathered material, probably because of slope processes that have affected the site during soil development. The amount of organic carbon in the topsoil of S7 is almost double to that found in S6. The H_2O_2 technique was able to extract the resilient organic matter present in the Bs2 horizon and thus to give an indication of the age of the profile. The detection of the resilient OM in the subsoil of S7, despite the proposed disruption of the site by slope instability, is evidence that the soil retains the memory of its development and that it can be considered as an archive of past geomorphological events and climatic conditions (Munroe, 2008).

The combination of the applied dating techniques in the soil profile S4 allowed the detection of increased periglacial activity/processes (solifluction) during a colder period around 2500 cal BP. This periglacial period would fit with the 'Göschener I' cold phase (around 3.0–2.3 ka; Zoller et al., 1966) (Fig. 5). Preweathered and mixed material, composed of different OM fractions (see Wang and Amundson, 1996), (having an age of 8400–9000 cal BP), was deposited on top of the original soil. This event initiated renewed soil development, as confirmed by clay mineral and mass balance investigations.

6. Conclusions

We used three relative and two absolute dating techniques to reconstruct landscape dynamics at the transition from the Pleistocene to the Holocene in a small Alpine catchment. We obtained the following findings:

- ^{10}Be ages agreed well with readvance phases of glaciers during the Younger Dryas and the Boreal (Oberhalbstein-/Schams-Kaltphase)
- Extraction and dating of resilient organic matter from Alpine soils (SOM) gave reliable ages about an ice-free surface and the first stages of soil organic matter formation. This technique offers new perspectives in deciphering landscape history but for a more

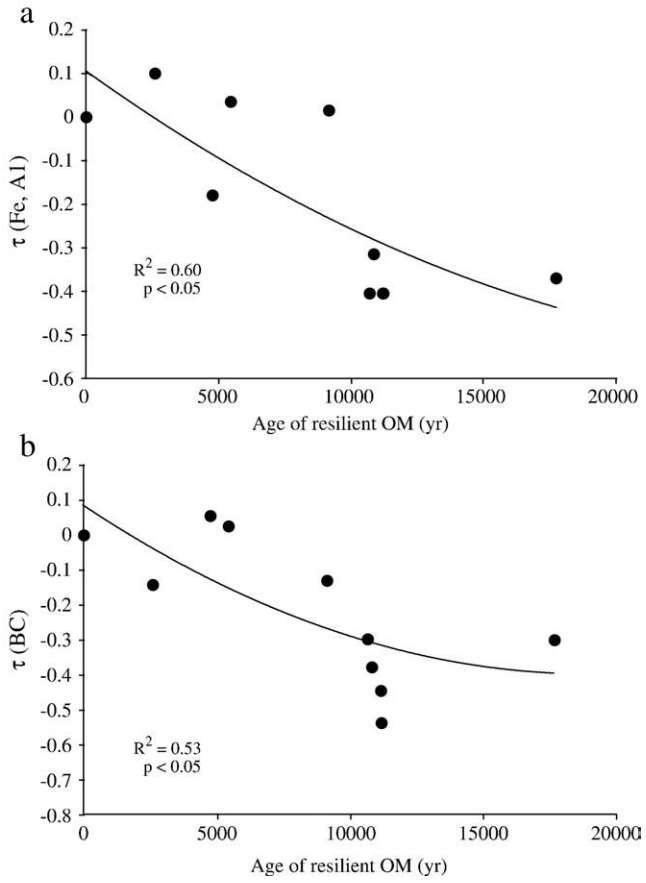

Fig. 7. Open system mass transport function $\tau_{j,w}$ as a function of the age of the soil profiles (^{14}C age) for the a) mean value of Fe + Al; b) mean value of base cations (BC = Ca, Mg, Na, K).

robust interpretation of the obtained ages, they have to be compared with other relative or absolute (numerical) dating techniques. In several cases, however, the oldest organic material could be found in the topsoil. This means that the top- and subsoil material has to be dated to obtain the oldest SOM fraction. Further research into the H_2O_2-resistant organic fraction is consequently needed, as is the development of new extraction methods.

- ^{10}Be and ^{14}C ages were in good agreement. Applied in combination with the chemical and physical characterisation of the surfaces, this procedure seems to be a promising tool for a better understanding of the geomorphology and palaeoclimate of relatively small catchments in Alpine environments. Soil formation usually started with a certain time-lag (around 0.5–1 ka) compared to the SED ages of the boulders (deposited in the Younger Dryas).
- The migration of pedogenic Fe and Al into the subsoil and the development of podzolic features are strictly bound to the surface stabilisation and to the duration of soil development.
- The production of clay minerals is time-dependent. The highest amounts of secondary minerals were found in the oldest soils. The amount of secondary minerals in the surface horizon is a useful tool to distinguish surfaces of different ages and to avoid misinterpretation of the ^{14}C ages (e.g., polygenetic soil S4). The clay mineral development supports the findings obtained by the chemical and physical soil characterisation (e.g., S6 and S7) and by the ^{14}C ages.
- The oldest soils were usually also the most-weathered. Consequently, the soil mass balance analysis indicated high elemental losses for old soils and low losses for young soils. Furthermore, this method enabled sites where soil evolution was disturbed due to slope instabilities to be detected (e.g. S6 and S7).
- Soils may keep the memory of their development. The present chemical and physical soil characteristics can be directly related to geomorphic process (e.g., solifluction, rock falls) occurring during the natural evolution of the area since the Lateglacial. The presence of charcoal fragments in the soil can also be used as a soil-age indicator.
- The approach used allowed a comparison of different dating methods and enabled an extended interpretation (by dating soils and boulders) and mutual control. Such an approach ultimately leads to a better understanding of landscape reconstruction and evolution.
- The obtained ages showed that Val di Rabbi experienced deglaciation between the end of the LGM and the end of the Boreal chronozones. The area was already deglaciated up to 2400 m asl around 14 000 yr ago in the NE-facing cirque. The southern part of the valley (south from Monte le Pozze) was deglaciated up to about 2500 m asl during the Bølling-Allerød chronozone (14 700–12 900 cal BP). At the end of the Egesen (11 600 cal BP), the western side of the transfluence pass (Passo Cercèn) was deglaciated up to 2600 m asl. In the eastern side of this pass, local glaciers remained until the onset of the Holocene climatic optimum (9000 cal BP). Several glacial oscillations and related processes (e.g., slope instability, solifluction) have affected parts of the region above 2400–2500 m asl during the Holocene, leaving clear and hidden (e.g., buried soil) evidence of their passage.

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Manuscript IV

Charcoal fragments of Alpine soils as the indicator of the landscape evolution during the Holocene in Val di Sole (Trentino, Italy)

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Charcoal fragments of Alpine soils as an indicator of landscape evolution during the Holocene in Val di Sole (Trentino, Italy)

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A HOLOCENE RESEARCH PAPER

Abstract: Subalpine and Alpine soils in Val di Sole (Trentino, Italy) have been investigated in order to reconstruct vegetation changes and human impact during the Holocene period. Archaeological findings have demonstrated that Alpine sites have been populated since pre-historical times. Humans have had a great impact on the natural landscape evolution. One of the most-used tools has been fire. The use of fire has enabled the landscape to be cleared to provide new pastures for grazing and also to allow it to be used for agricultural purposes. The ^{14}C dating of charcoal fragments found in subalpine and Alpine soils provide information about the type of vegetation, fires, human impact and soil formation throughout the Holocene. The degree of podzolisation indicates weathering effects and provides information about the stability of the surfaces. According to our results, a quick forest expansion establishment phase must have occurred shortly after the Lateglacial around 10 500 cal. BP. *Pinus sylvestris*, *Pinus mugo* as well as *Larix decidua* established in the investigation area in that period. *Picea abies* had not yet migrated into this region at the transition to the Boreal (around 9000 cal. BP). The vegetation of the investigated area has not substantially changed during the last 10 000 years. *Pinus mugo* was more widespread in some areas during the Older Atlanticum, and the treeline was about 150 m higher at the end of the Younger Dryas than today. Some other sites were most probably used as pasture during the Bronze Age and later abandoned, leading to a natural reforestation. In the investigated area 13 fire events in the past 10 700 years have been recognised, and seven of them can reasonably be attributed to human origin.

Key words: Alps, charcoal, soils, Holocene, anthracology, ^{14}C.

Introduction

The Alpine landscape has been shaped by the movements of the glaciers during the period of ice retreat at the end of the last glacial maximum (LGM, *c*. 24 000–21 000 cal. BP; Kelly *et al*., 2004). The oscillations of the climatic conditions during the Lateglacial have influenced the species composition of the vegetation. After the first retreat of the glaciers, during the Oldest Dryas chronozone (Maisch *et al*., 1999), the Alps were characterised by tundra and steppe species such as *Dryas octopetala* L., *Ephedra* L., *Artemisia* L., Poaceae R.Br. and Chenopodiacae Vent. (Burga and Perret, 1998). The subsequent periods of warm and cold phases have caused vegetation changes and seen the progressive establishment of species that are nowadays very typical of the Alpine environment such as *Larix decidua* L., *Pinus cembra* L., *Juniperus* sp. L. and *Picea abies* L. (Wick, 1989; Burga and Perret, 1998). Past environments and climate have been reconstructed by many authors through the identification and dating of sedimentary pollen deposited in peat bogs or in Alpine lakes (ie, Kral, 1971; Wegmüller, 1977; Pini, 2002; Gobet *et al*., 2004; Filippi *et al*., 2005; Finsinger *et al*., 2007; Favaretto *et al*., 2008; Jimenez-Moreno *et al*., 2008). The assemblages of pollen grains are directly related to regional and local vegetation. The success of pollen in determining past climatic conditions is strongly dependent on high-quality modern calibration data for establishing the relationship between vegetation, pollen assemblages and climatic parameters (Birks, 2004).

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Another powerful tool used to reconstruct past environments and climate is the extraction, identification and radiocarbon dating of macrofossil charcoal fragments buried in Alpine soils. All forest ecosystems have the potential to burn as a result of climate- or human-induced fires (Figueiral and Mossbrugger, 2000). Macrofossil charcoal is organic plant material (fragments > 2 mm diameter), that is a C-enriched, N-depleted pyrogenic substance having a highly aromatic structure, preserved in the fossil record through the process of incomplete burning and charcoalification (Schweingruber, 1978, 1990; DeLuca and Aplet, 2008). Charcoal fragments > 2 mm usually remain on the fire site or in the immediate vicinity (Lynch *et al.*, 2004). Charcoal fragments are particularly useful for the identification of fossil wood because the level of preservation is often good enough to examine the transversal, longitudinal and tangential sections of the wood and thus, using this knowledge of the wood structure of the charcoal, to establish the identity of the tree from which it came to the genus (and in some cases to the species) level. The presence of carbonised fragments of wood is clear evidence of the occurrence of a fire, and of the capability of the environment to supply the necessary conditions for the growth of trees belonging to a certain botanical species. Those include an ice-free and in most places permafrost-free terrain, a soil able to support woody vegetation, and extremes of climate that do not exceed the physiological capabilities of the tree taxa (Willis and van Andel, 2004). Moreover, charcoal is often suggested as the most reliable material for radiocarbon dating from archaeological sites (Damblon and Haesaerts, 1997). Charcoal fragments are biologically inert and physically stable within the environment (Pessenda *et al*., 2001). Furthermore, soil charcoal dating gives a time proxy for soil pedogenesis (Carcaillet, 2001) and can be used to estimate soil age. Charcoal fragments have been widely used especially in studies about treeline shifting, soil pedogenesis, fire regimes, changes in vegetation and carbon storage (eg, Berli *et al*., 1994; Cherubini *et al*., 1995; Carcaillet and Brun 2000; Carcaillet, 2001; Carnelli *et al*., 2004a; Ali *et al*., 2005; Hajdas *et al*., 2007; Bélanger and Pinno, 2008; DeLuca and Aplet, 2008). Charcoal identification and dating is a powerful tool to reconstruct past human impact on Alpine territories. Although natural fire regimes appear to be climate-dependent, human activity at the forest- and treeline in the Alps has been occurring for thousands of years (Whelan, 1995; Carcaillet, 1998; Carcaillet *et al*., 2007). If fire patterns are synchronous at regional scales, then they should be reasonably ascribed to climatic trends: but, if they are not synchronous at regional scales, then fire regimes might be more dependent on local processes such as human disturbance (Clark and Royal, 1995). Charcoal fragments allow the reconstruction of Quaternary landscapes and environments and the identification of natural or human disturbance on vegetation (Figueiral and Mosbrugger, 2000). According to the geomorphological studies of Baroni and Carton (1990), Filippi *et al*. (2007) and Favilli *et al*. (2009), the formation of the present landscape can be dated back between 18 000 and 11 000 yr cal. BP. Studies of human remains (teeth and bones) have dated the first modern-humans settlements in the Trentino region back to 14 000 years ago (Di Benedetto *et al.*, 2000). Archaeological studies have demonstrated the continuous presence of complex human societies in these valleys from the Mesolithic period (*c*. 8000–4500 cal. BP) until modern history (eg, Cucina *et al.*, 1999; Schmidl *et al.*, 2005; Valsecchi *et al.*, 2006).

This study focuses on the identification and dating of charcoal fragments extracted from nine Alpine and sub-Alpine soils. The obtained ages have been compared with archaeological studies done in nearby Alpine valleys to derive a continuum of the human activities in the sub-Alpine and Alpine territories of Trentino (Italy). An additional aim of this research was to relate the age of the charcoal fragments to soil development (see also Zech *et al*., 2003). This work will also show the importance of Alpine soils as natural archives of past events and climatic shifting.

Materials and methods

Study area and investigation sites

The investigated sites are located in Val di Pejo and Val di Rabbi, two lateral valleys of Val di Sole, Trentino, in the southern Alpine belt of northern Italy (Figure 1). The climate of the valleys ranges from temperate to alpine (above the treeline). Mean annual temperature ranges from 8.2°C (valley floor–800 m a.s.l.) to around 0°C (at 2400 m a.s.l.) and mean annual precipitation approximately from 800 to 1300 mm (Servizio Idrografico, 1959). The treeline is *c*. 2100 m a.s.l. and the forests are dominated by the conifers *Larix decidua* L. and *Picea abies* L. (Pedrotti *et al*., 1974). Areas above 2300 m are covered with rocks, boulders and short-grass meadows dominated by *Carex curvula* L. and *Nardus stricta* L. The siliceous parent material (paragneiss and micaschists) and the coverage by quaternary deposits are similar in both valleys (Table 1). We investigated nine soil profiles developed in the sub-Alpine and Alpine zone on different morphological aspects with respect to their evolution. Furthermore, charcoal fragments extracted from each soil profile were identified and radiocarbon dated. The investigated soils (Table 1 and Figure 1) were between 1521 m a.s.l. and 2222 m a.s.l., and therefore, in the sub-Alpine and in the Alpine zone (Egli *et al*., 2008) above the treeline. The whole landscape near the investigation area was strongly influenced by glaciers and later by human activities.

Soils were classified as *Entic Podzol* between 1500 and 1600 m a.s.l., *Cambic Umbrisol* between 1600 and 1800 m a.s.l., *Haplic Cambisol* and *Entic Podzol* between 1800 and 2200 m a.s.l. according to the WRB (IUSS Working Group, 2007). According to the Soil Taxonomy (Soil Survey Staff, 2006), the soil moisture regime is udic (humid conditions, <90 days/year with a dry soil) at all sites. Maximum precipitation occurs during the summer months.

Sampling

The sampling strategy was based first on the opening of the soil profiles and on the subsequent soil description. Undisturbed soil samples were collected from excavated pits starting from the BC horizon upward to avoid contamination of the soil material. A total of 2 to 4 kg of soil material were collected per soil horizon at the nine soil pits (Hitz *et al*., 2002). Large charcoal fragments were separated from the soil matrix directly on the field.

Soil chemistry and physics

The samples were air-dried, large aggregates were gently broken by hand and sieved to < 2 mm. Total C and N contents of the soil were measured with a C/H/N analyser (Elementar Vario EL, elementar Analysensysteme GmbH) using oven-dried and ball-milled fine earth. Soil pH (in 0.01 M $CaCl_2$) was determined using air-dried samples of fine earth having a soil solution ratio of 1:2.5. The oxalate-extractable (Fe_o, Al_o) fraction was extracted according to McKeague *et al.* (1971) and analysed by AAS (Atomic Absorption Spectrometry – AAnalyst 700, Perkin Elmer, USA). The carbon and the charcoal stock in each soil profile were calculated according to the amount of organic carbon and of charcoal fragments, the density and the thickness of the soil horizons.

Charcoal identification and analysis

Macrocharcoal fragments having a diameter larger than 2 mm were extracted from the soil matrix by hand, strained through a sieve and dried at 40°C. The individual fragments were analysed

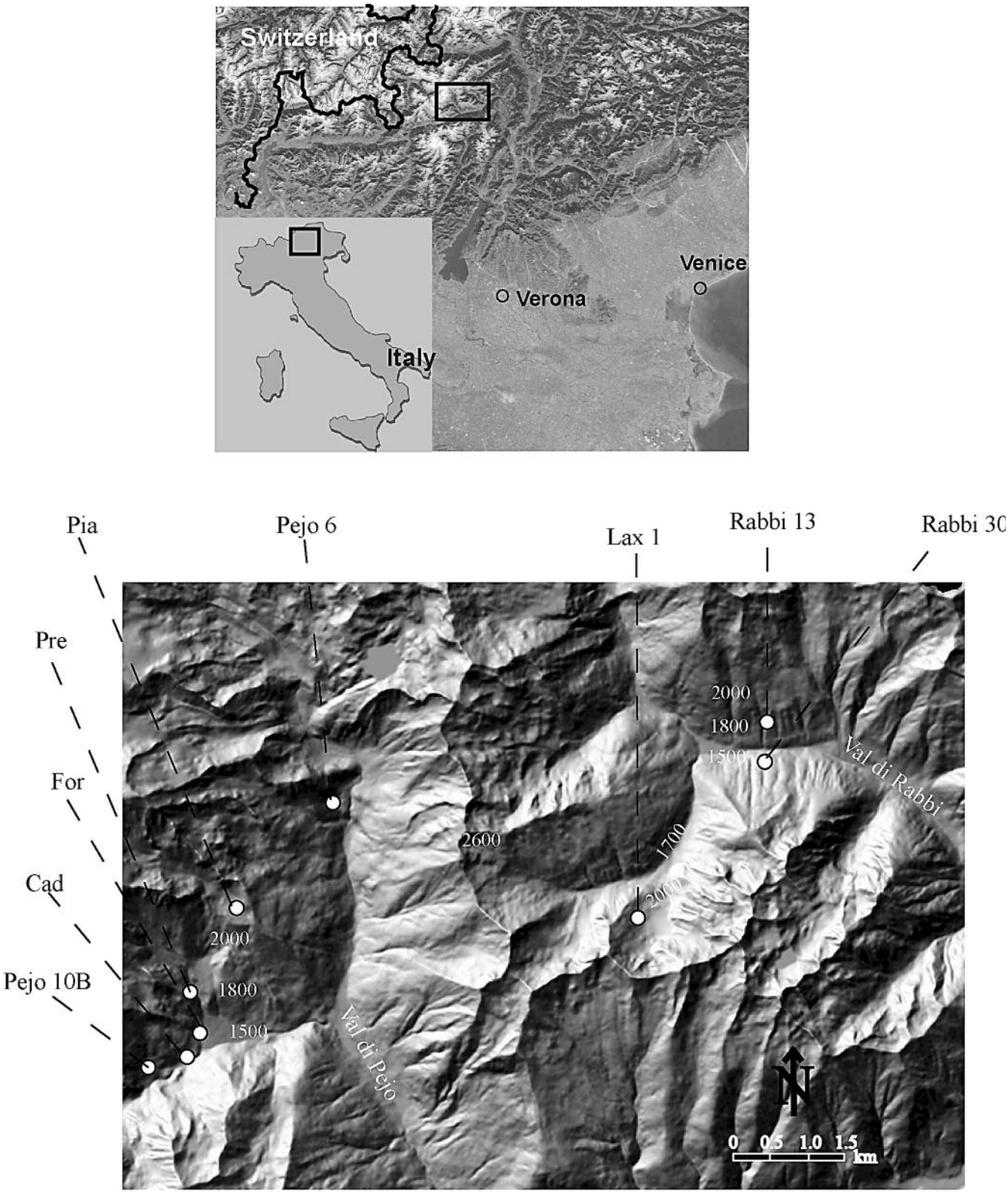

Figure 1 Location of the investigation site

microscopically and separated into coniferous and broadleaved tree species (Schoch, 1986) with a stereomicroscope (magnification 6.4–40×, Wild M3Z Leica, Germany). The charcoal fragments from the coniferous trees were divided further at the genus level using a reflected-light microscope (objective 5×, 10× and 20×, Olympus BX 51, Japan). The observations were compared with a histological wood-anatomical atlas, using an identification key (Schweingruber, 1990).

Radiocarbon dating

The CO_2 of the combusted samples was catalytically reduced over cobalt powder at 550°C to elemental carbon (graphite). After the reduction, this mixture was pressed into a target and carbon ratios were measured by Accelerator Mass Spectrometry (AMS) using the tandem accelerator of the Institute of Particle Physics at the Swiss Federal Institute of Technology Zurich (ETHZ). The calendar ages were obtained using the OxCal 4.0.5 calibration program

Table 1 Characteristics of the study site

Soil profile	Elevation (m a.s.l.)	Aspect (°N)	Slope (%)	Parent material	Vegetation	Land use	WRB (IUSS WRB, 2007)
Cad	1521	275	18	Micaschists	*Larix decidua / Picea abies*	Natural forest	Entic Podzol
Rabbi 30	1600	25	43	Paragneiss	*Larix decidua / Picea abies*	Natural forest	Entic Podzol . (Endoskeletic)
For	1621	350	12	Micaschists	*Larix decidua / Picea abies*	Natural Forest	Cambic Umbrisol
Pejo 6	1630	120	70	Micaschists	*Larix decidua / Picea abies*	Natural forest	Cambic Umbrisol
Pejo 10B	1810	130	70	Micaschists	*Larix decidua / Picea abies*	Natural forest	Haplic Cambisol (Dystric)
Pre	1818	305	5	Micaschists	*Larix decidua*	Natural Forest	Entic Podzol
Rabbi 13	1860	185	65	Micaschists	*Picea abies / Larix decidua*	Natural forest	Haplic Cambisol (Dystric)
Lax 1	2083	240	32	Paragneiss	*Larix decidua / Picea abies*	Natural forest	Entic Podzol
Pia	2222	350	21	Micaschists	*Rhododendro – vaccinietum extrasilvaticum*	Natural grassland and shrubs	Haplic Cambisol (Dystric)

(Bronk Ramsey, 1995, 2001) based on the IntCal 04 calibration curve (Reimer *et al*., 2004). Calibrated ages are given in the 2 σ range (minimum and maximum value).

Results

Physical characteristics and chemical composition of the soils

The investigated soils developed on paragneiss or micaschists containing morainic till (Table 1). The proportion of rock fragments increases with soil depth (Table 2), showing typical values for Alpine soils developed on a morainic sediment (Egli *et al*., 2001). All investigated soils have a loamy to loamy-sand texture. Because of the acidic characteristics of the parent material, the soils show pronounced acidification (Table 2). Total C corresponds to organic C because of the absence of any carbonates in the soil. The C stock is higher in the N-exposed soils located below 1800 m a.s.l. (Table 2).

The soils ('Cad', 'Rabbi 30', 'Pre', 'Rabbi 13' and 'Lax 1') showed a pronounced podzolisation, as shown by the clear increase in the oxalate-extractable iron and aluminium contents measured in all spodic horizons (Figure 2 and Table 2). Chemical criteria for spodic material require that oxalate-extractable Al_o + 0.5 Fe_o is ≥ 0.5% and at least two times greater than in the overlying albic horizon (Soil Survey Staff, 2006; Briggs *et al.,* 2006). In our studied soils, the average Al_o + 0.5 Fe_o value in the Bs (or Bs1 or Bs2) horizon is 0.94 (%wt) and 0.47 (%wt) in the AE (or BE) horizon.

The soils 'For' and 'Pejo 6' developed at 1600 m a.s.l. and on the same parent material. The soil 'For' developed on a north-facing slope most probably near a former charcoal pile in a coniferous forest. This soil is only 50 cm deep and correspondingly weakly developed. The first 25 cm contained large charcoal fragments. Therefore, the level of charcoal preservation is very good and the topsoil is extremely rich in organic carbon, which decreases substantially in the subsoil (Table 2). The stock of C is mostly due to the big charcoal accumulation as a charcoal pile. The chemical evolution indicates an initial downward movement of Fe and Al (Figure 2). The Al_o + 0.5 Fe_o value in the Bs horizon is 0.78% which is consistent with an on-going podzolisation (Table 2) (Soil Survey Staff, 2006; Briggs *et al*., 2006). The soil 'Pejo 6' developed on a south-facing slope and shows a more pronounced development of horizons. Fe and Al migrated and accumulated in the BA horizon. The AE and BA horizon had a dark brownish-black colour. The horizons differed in the soil skeleton, the organic matter content and in the pH. The two subsoil horizons (Bs and BC) were very similar. Both present a brown colour (7.5YR 4/4 and 10YR 4/4) and a higher pH. The organic matter content decreases clearly in the subsoil. 'Pejo 10B' developed on a south-facing slope under a coniferous forest and had a layer at around 75 cm depth that was particularly enriched with charcoal fragments. This enrichment is also indicated by the higher amount of organic C in the BC horizon (Table 2). The oxalate-extractable Fe and Al shows an increase with depth throughout the profile owing to the continuous differentiation of the horizons. In the soil profile 'Pia', an initial migration of iron and aluminium can also be measured.

Charcoal identification and age

Charcoal fragments occurred in all investigated soils. We dated 23 charcoal fragments extracted from different soil profiles. The ratios of the weight of the macrocharcoal fragments to the total weight of the sampled soil material can themselves give an indication of the age of the charcoal. Coarse charcoal particles derive from deadwood and downed wood, stumps or dead roots. Microcharcoal is related to fine plant material (eg, grass) or to the physical breakdown of macrocharcoal (DeLuca and Aplet, 2008). The presence of young and well-preserved carbonised wood in the soil horizons can be indicated by a charcoal/soil weight ratio > 0.4 (Table 3). A better preservation of carbonised young wood implies a modern age of the fragments. Over time, a part of the macrocharcoal can decay or is physically reduced in size. A positive and significant correlation between the percentage of macrocharcoal and the ^{14}C age was also found (Figure 3).

The age of the charcoal fragments spans more than 10 000 years, between 1799–1894 cal. AD and 8844–8429 cal. BC (10 378–10 793 cal. BP) (Table 3). The oldest charcoal fragments were found in the deepest soil horizons, in accordance with the assumption of the stratification of wood charcoal in soil (Berli *et al.*, 1994; Carcaillet, 2001) (Figure 4). Since the soils are acidic and have, if any, only a weak (endogeic) earthworm activity, bioturbation has been negligible. Old charcoal could move downward in the profile due to trapping in the plant-root network.

Table 2 Chemical and physical characteristics of the investigated soils

Site	Soil horizon	Depth (cm)	Munsell colour (moist)	Skeleton[a] (weight %)	pH ($CaCl_2$)	Org. C (g/kg)	Total N (g/kg)	C/N	Al_o (g/kg)	Fe_o (g/kg)	Al_o+ 0.5 Fe_o (%)	C Stock (t/ha)	Charcoal (t/ha)
Cad													
	O	0–12	7.5YR 3/3	11	4.2	161.9	10.4	15	–	–	–	98.2	0.35
	AE	12–20	7.5YR 3/4	18	4.0	55.5	3.5	15	1.41	4.85	0.38	21.4	4.27
	BA	20–35	7.5YR 4/6	17	4.1	30.4	1.7	18	4.27	7.68	0.81	36.1	3.45
	Bs1	35–45	10YR 4/6	21	4.2	16.5	0.9	17	2.26	2.63	0.36	14.3	0.31
	Bs2	45–70	7.5YR 5/6	29	4.3	17.2	0.9	19	1.24	2.46	0.24	34.3	0.45
Rabbi 30												∑: 204.3	∑: 8.83
	AE	18–25	10YR 1.7/1	30	3.0	103.5	5.0	21	3.66	3.36	0.53	228.2	-
	Bs1	25–50	7.5YR 4/3	50	3.4	59.0	2.6	23	5.21	10.52	1.05	56.1	-
	Bs2	50–60	5YR 3/3	60	3.7	87.3	3.9	22	10.35	18.22	1.95	37.0	-
	BC	60–90	10YR 4/6	70	3.9	63.1	2.2	29	10.1	15.61	1.79	90.9	-
For												∑: 412.2	
	OE	0–25	10YR 1.7/1	20	3.9	137.6	4.1	34	3.02	5.06	0.55	221.0	239.10
	Bs	25–50	7.5YR 4/6	32	4.2	25.7	1.2	21	4.37	6.85	0.78	47.4	8.37
Pejo 6												∑: 268.5	∑: 247.47
	AE	0–10	7.5YR 3/2	10	3.8	115.1	6.2	19	2.02	5.41	0.47	109.8	–
	BA	10–35	7.5YR 3/2	15	4.0	36.3	13.3	3	3.90	7.37	0.76	58.6	–
	Bs	35–58	7.5YR 4/4	15	4.6	12.4	1.2	10	3.62	4.83	0.61	17.2	–
	BC	58–85	10YR 4/4	35	4.7	7.6	0.6	11	1.62	4.45	0.38	22.0	–
Pejo 10B												∑: 207.7	
	A	4–10	7.5YR 3/2	10	3.9	46.8	2.4	19	2.37	6.17	0.55	19.8	–
	Bs1	10–50	7.5YR 4/3	30	4.0	14.6	0.6	24	2.71	6.53	0.59	49.9	–
	Bs2	50–70	5YR 3/2	50	4.3	16.1	0.6	27	3.09	7.62	0.69	18.8	–
	BC	70–80	10YR 4/4	60	4.3	72.3	2.0	36	7.06	10.77	1.24	36.7	–
Pre												∑: 125.2	
	A	0–3	10YR 3/2	20	3.9	62.4	3.6	17	1.61	5.11	0.42	8.4	0.01
	AE	3–12	10YR 4/4	45	4.1	30.7	1.8	17	1.83	5.46	0.46	14.5	0.44
	Bs	12–45	10YR 5/4	47	4.7	17.8	1.2	17	6.98	9.15	1.15	38.9	0.05
	BC	45–60	10YR 4/6	38	4.8	7.5	0.5	14	3.20	4.31	0.23	8.7	0.97
Rabbi 13												∑: 70.6	∑: 1.47
	AB	3–10	10YR 4/4	10	4.2	24.4	0.6	40	2.15	4.66	0.45	21.7	–
	Bs1	10–37	7.5YR 4/6	15	4.3	20.2	0.8	25	2.68	4.44	0.49	51.9	–
	Bs2	37–55	7.5YR 4/6	25	4.9	10.3	0.7	15	4.47	4.88	0.69	18.1	–
	BC	55–100	2.5YR 5/4	45	5.0	4.3	0.4	11	2.08	1.05	0.26	15.2	–
Lax 1												∑: 107.0	
	AE	5–11	10YR 4/3	7	3.5	56.9	2.7	21	2.18	7.13	0.57	–	–
	Bs1	11–26	5YR 4/6	16	3.8	35.3	1.7	21	6.42	20.19	1.65	–	–
	Bs2	26–50	7.5YR 4/6	47	4.3	22.8	1.1	21	6.35	10.08	1.14	–	–
Pia													
	AE1	0–8	7.5YR 3/2	19	4.6	75.8	4.4	17	–	–	–	24.6	0.12
	AE2	8–11	7.5YR 4/3	19	4.4	52.4	3.3	16	1.49	5.04	0.41	8.3	0.05
	BE	11–25	7.5YR 4/4	12	4.3	14.4	0.9	15	1.38	5.05	0.39	14.9	0.50
	Bs1	25–55	7.5YR 4/6	26	4.5	8.7	0.6	14	1.87	5.46	0.46	22.0	0.39
	Bs2	55–80	10YR 4/6	29	4.7	7.1	0.5	15	1.66	4.48	0.39	16.1	0.27
												∑: 85.9	∑: 1.33

[a] Skeleton = material > 2 mm.

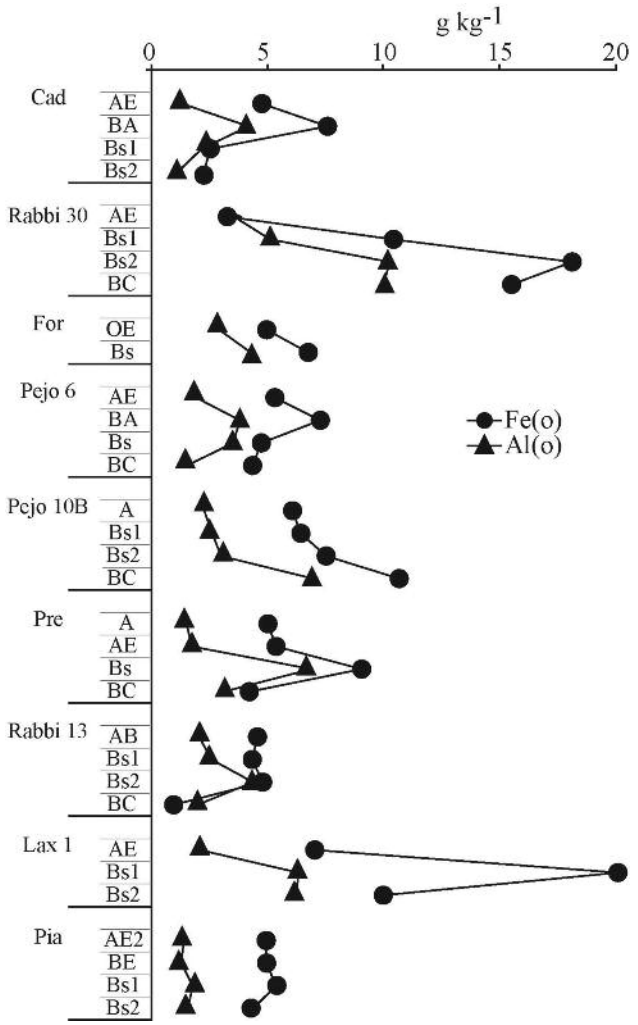

Figure 2 Migration of Fe and Al (dithionite extraction) in the investigated soil profiles

In general, vegetation did not dramatically change during the last 10 000 years. The charcoal fragments mostly belong to *L. decidua, P. abies, Clematis* spp. and Ericaceae – trees and bushes which also dominate the present-day forest (Table 3). The differentiation was not possible between *Picea* and *Larix* species based on the wood anatomy (Schweingruber, 1978). Some fluctuations can, however, be observed in the charcoal composition within the individual soil profiles (Figure 5).

The charcoal fragments of the profile 'Cad' (1521 m a.s.l.) in the Bs1 horizon were identified as *Clematis* sp.; most probably it belongs to the Alpine variety of this plant, in the family Ranunculacae (*Clematis alpina* (L.) Mill.). This plant is typical of a sub-Alpine forest in the sub-association *Rhododendro-Vaccinietum cembretosum* in the mesophylous *Pinus cembra* forests on the cooler aspects (Motta and Nola, 2001).

Other charcoal fragments in the Bs2 horizon of 'Cad' and in the Bs1 of 'Pejo 10B' belong to the Ericaceae family, which also includes species such as *Rhododendron, Vaccinium* and *Calluna*, which are common in the sub-Alpine forest (Carnelli *et al*., 2004b).

The vegetation currently present at the site 'For' (1621 m a.s.l.) is a *P. abies/L. decidua* forest. The charcoal fragments in the soil indicate that a vegetation change took place in the past. Charcoals of *L. decidua*, *P. abies*, *Alnus* sp. and *Betula* sp. were found in the soil profile. About half of the charcoals derive from coniferous and the other half from deciduous trees, which are now absent from the site.

The site 'Pre' (1818 m a.s.l.) shows a change from a *Pinus sylvestris or Pinus mugo* dominated forest (beginning of the Preboreal) to a *Picea* or *Larix* forest. The oldest charcoal fragments of the 'Pia' soil profile (2222 m a.s.l.) also evidenced a change from a *Pinus sylvestris or Pinus mugo* dominated forest to a *Picea*/*Larix* forest and an early-Holocene coniferous forest above the present-day treeline.

According to the radiocarbon age of the charcoal fragments, several fire phases can be recognised. The sites located at low altitudes (1500–1700 m a.s.l.) showed a predominance of charcoal fragments in the period 1399–1894 cal. AD, that can be attributed to the Middle Ages and Modern history. Some fragments refer to the Bronze Age (1450–825 cal. BC) and to the Roman Time period (119–253 cal. AD) (Table 3).

In the altitudinal range 1800–2000 m a.s.l., we detected a higher number of older charcoal fragments with a peak in the Bronze Age (*c.* 2300–600 cal. BC, Schmidl *et al*., 2005). Only few recent charcoal fragments (Modern history) were found in the top horizons.

The soils located > 2000 m a.s.l. showed some very old charcoal fragments (around 10 000 years) in the subsoil, with only a few fragments in the Bronze Age or Middle Ages. No fragments of the Modern history period were found.

In the investigated area and sites, no charcoal fragments were found having an age between 8200 and 3300 cal. BC. A fire synchronicity could be observed for the periods around 8500 cal. BC (10 500 cal. BP), 1400–1800 cal. BC (3350–3750 cal. BP), ~1420 cal. AD (600–1000 cal. BP) (Figure 6). The other fires referred to isolated dates and are probably human-induced.

Discussion

Fire regimes and human impact

Fire regimes are influenced by the presence of vegetation, favourable climatic conditions and human activities. Several fire events or sequences occurred simultaneously at different sites. This synchronicity may be used as an indication of climate forcing (Carcaillet *et al*., 2007).

We consider the following time periods for a better explanation of the fire events at our sites (Figure 7):

(1) early Holocene (8900–8200 cal. BC)
(2) Copper, Bronze and early Iron Age (4300–400 BC)
(3) late Iron Age, Roman Time and Middle Ages (400 BC–AD1400)
(4) Modern history (> AD 1400)

(1) Early Holocene (8900–8200 BC) (Figure 7a)

Some very old charcoal fragments (8900–8200 cal. BC) were found in the soils at the highest elevations (1818–2222 m a.s.l.) and can be attributed to the transition of the Egesen glacier readvance phase to the Preboreal phase (11 600–10 200 cal. BP; Maisch *et al*., 1999; Ivy-Ochs *et al*., 2006, 2008; Favilli *et al*., 2008, 2009). According to pollen studies in nearby lakes (Pini, 2002; Filippi *et al*., 2005), the immigration of *P. sylvestris* and *P. mugo* occurred around 13 000 cal. BP at 700 m a.s.l. and the increase in xerophytes plants suggests the onset of a dry climate after the Younger Dryas. This change in climatic conditions could be responsible for the occurrence of natural fires in this period. Pollen studies indicated that *P. cembra*, *L. decidua* and *Betula pubescens* grew locally at 2200 m a.s.l. around 9300 cal. BP (Wick and Tinner, 1997). The three charcoal fragments extracted from the alpine soils ('Pia', 'Pre' and 'Lax 1') confirmed the early-Holocene establishment of the forest (*L. decidua, P. sylvestris* and *P. mugo*) and evidenced fires *c*. 10 500 years ago in

Table 3 Measured and calibrated radiocarbon ages of charcoal fragments > 2 mm. Calibrated ^{14}C ages are given in the 2 σ range

Site	Soil horizon	Depth (cm)	Identified charcoal fragments	Dated charcoal fragment	Macrocharc g/kg soil	Uncal ^{14}C	Cal ^{14}C BP	Calendar age (years BC/AD) and prehistoric civilization
Cad								
	O	0–12	*Picea/Larix*	–				
	AE	12–20	*L. decidua*[a]	–				
	BA	20–35	*L. decidua*	–				
	Bs1	35–45	*Larix/Picea*	Clematis	0.3	3090 ± 50	3205–3405	1456–1256 BC Bronze Age
	Bs2	45–70	*L. decidua*	*Ericaceae*	0.1	4550 ± 55	5038–5327	3378–3089 BC Copper Age
Rabbi 30								
	AE	18–25	*L. decidua*	*L. decidua*	3.3	495 ± 30	500–551	1399–1450 AD Modern
	Bs1	25–50	*L. decidua*	*L. decidua*	0.3	1830 ± 30	1698–1831	119–253 AD Roman Time
	Bs2	50–60	*L. decidua*	*L. decidua*	0.1	2755 ± 35	2774–2929	825–980 BC Bronze Age
	BC	60–90	–	–				
For								
	OE	0–25	*Alnus* sp.	*L. decidua*	89.3	240 ± 45	260–334	1616–1691 AD Modern
			Betula sp.	*L. decidua*		185 ± 45	124–231	1719–1826 AD Modern
	Bs	25–50	–	–				
Pejo 6								
	AE	0–10	*L. decidua*	*L. decidua*	2.2	130 ± 30	57–152	1799–1894 AD Modern
	BA	10–35	*L. decidua*	*L. decidua*	0.7	150 ± 30	167–233	1718–1734 AD Modern
	Bs	35–58	*L. decidua*	*L. decidua*	0.7	480 ± 30	498–543	1407–1453 AD Modern
	BC	58–85	–	–				
Pejo 10B								
	A	4–10	*Larix/Picea*	*L. decidua*	3.1	375 ± 30	424–505	1446–1527 AD Modern
	Bs1	10–50	*Ericaceae*	*Ericaceae*	0.3	3100 ± 35	3239–3390	1441–1290 BC Bronze Age
	Bs2	50–70	–	–				
	BC	70–80	*Larix/Picea*	*Larix/Picea*	9.7	3460 ± 35	3640–3831	1882–1691 BC Bronze Age
				Larix/Picea		3445 ± 35	3631–3832	1883–1682 BC Bronze Age
Pre								
	A	0–3	–	–				
	AE	3–12	*Picea/Larix*	*Picea/Larix*	0.2	1135 ± 50	937–1174	776–1031 AD Middle Age
	Bs	12–45	–	–				
	BC	45–60	*P. sylvestris*[b]	*P. sylvestris*	0.1	9385 ± 75	10378–10793	8844–8429 BC Early Holocene
Rabbi 13								
	AB	3–10	*L. decidua*	*L. decidua*	0.4	510 ± 30	505–555	1395–1445 AD Modern
	Bs1	10–37	*L. decidua*	*L. decidua*	0.1	1725 ± 30	1557–1708	243–393 AD Roman Time
	Bs2	37–55	–	–				
	BC	55–100	–	–				
Lax 1								
	AE	5–11	*Larix/Picea*	*Larix/Picea*	n.d.	3055 ± 50	3081–3381	1432–1192 BC Bronze Age
	Bs1	11–26	*Larix/Picea*	*Larix/Picea*	n.d.	3065 ± 55	3080–3393	1444–1191 BC Bronze Age
	Bs2	26–50	*Larix/Picea*	*Larix/Picea*	n.d.	9160 ± 70	10212–10509	8560–8263 BC Early Holocene
Pia								
	AE1	0–8	–	–				
	AE2	8–11	–	–				
	BE	11–25	*Pinus/Larix*	*Pinus/Larix*	0.1	1220 ± 50	1054–1277	674–897 AD Middle Age
	Bs1	25–55	–	–				
	Bs2	55–80	*Pinus/Larix*	*P. sylvestris*	0.1	9340 ± 75	10293–10734	8785–8344 BC Early Holocene

– = no charcoal fragments/size < 1 mm
n.d. = Not determined
[a]*L. decidua = Larix decidua*
[b]*P. sylvestris = Pinus sylvestis*

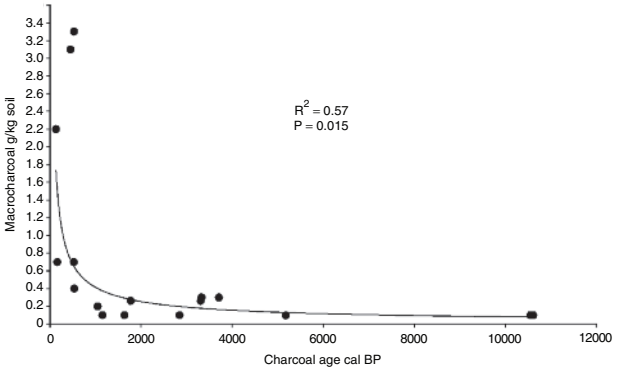

Figure 3 Correlation between the macrocharcoal weight in soil and the calibrated ^{14}C ages of the charcoal fragments

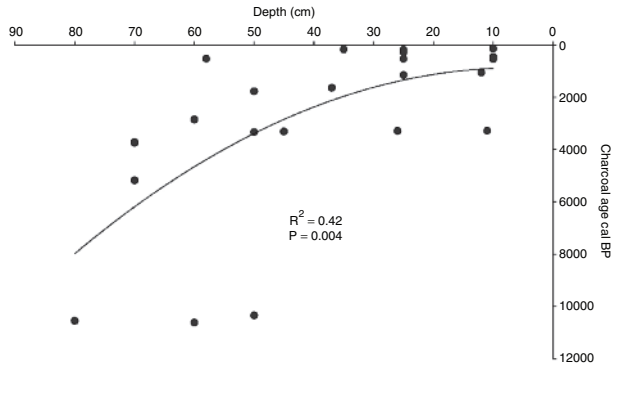

Figure 4 Relationship between the age of the charcoal fragments and soil depth (using second order polynomial regression)

a wider area (Figures 1 and 7a). During the early Holocene, the treeline reached altitudes of around 2200–2300 m a.s.l. (Burga and Perret, 1998; Dalmeri *et al*., 2007). The climate was generally slightly warmer than today in the period from the Preboreal until the beginning of the Bronze age (Burga and Perret, 1998). *P. sylvestris, P. mugo* and *L. decidua* were present in the mixed coniferous forest (Pini, 2002), which is in accordance with the change in vegetation found at the highest sites (Figure 5). The charcoal fragment extracted from the soil 'Pia' at 2222 m a.s.l. evidenced a downward shifting of the treeline by about 150 m from the early Holocene to the present. Several studies carried out in the French Alps (eg, David, 1993), in Scotland (Pears, 1968) and in Switzerland (Carnelli *et al*., 2004a), have demonstrated that during the Preboreal and Boreal period (*c*. 9500–7000 cal. BP; Maisch *et al*., 1999) the treeline was about 200–250 ± 100 m higher than today.

Preconditions for forest fires are the presence of a substantial amount of flammable conifers, a relatively dry climate or periods with drought and thunderstorms (lightning). Such conditions were obviously prevalent at the beginning of the Preboreal. High elevation woodlands have been dominated by relatively flammable conifers since 8000 cal. BP (David, 1995; Carcaillet

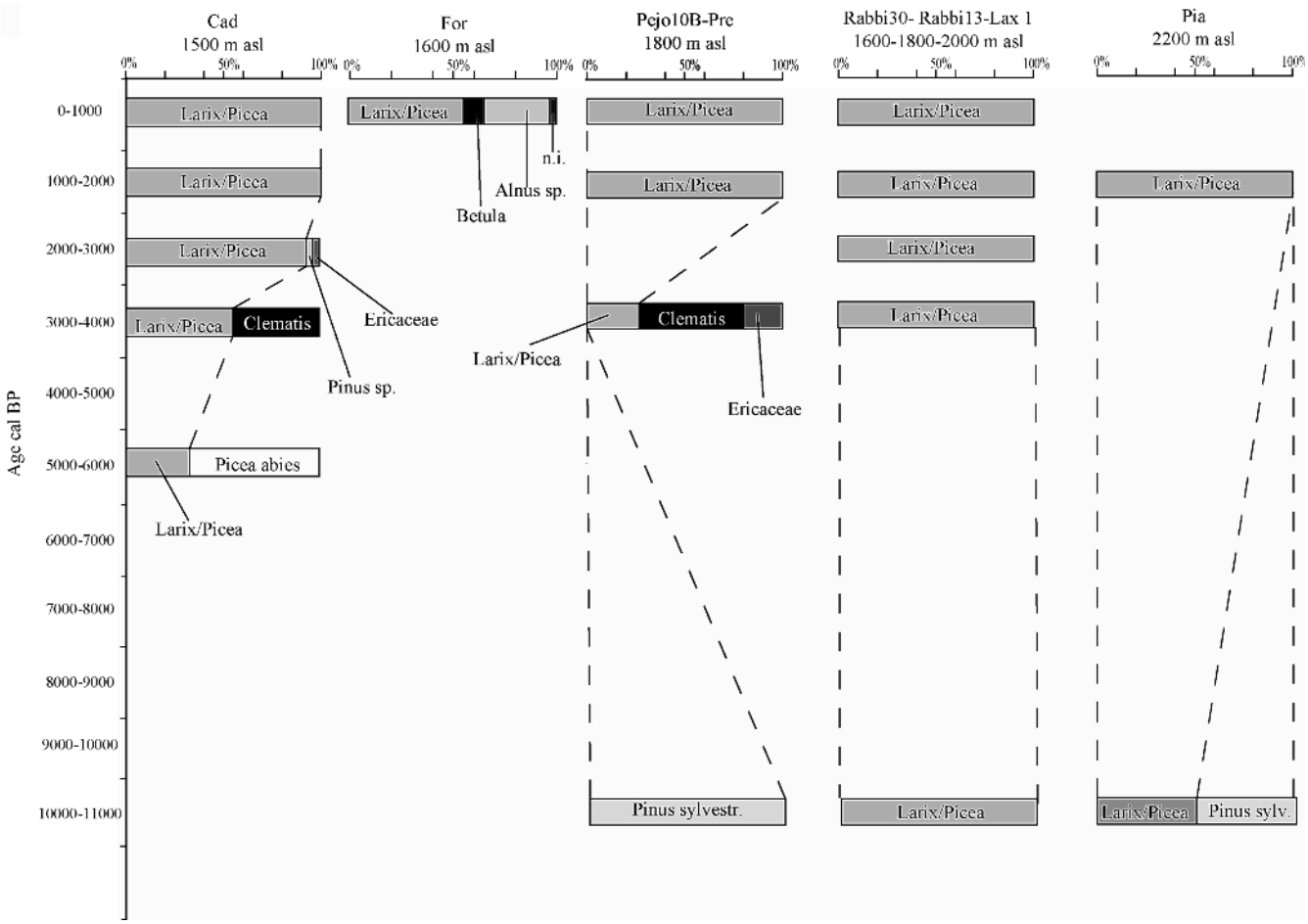

Figure 5 Composition of the vegetation as a function of time derived from charcoal fragments in the soils (up to 107 charcoal fragments per soil horizon were analysed). Some soils having a similar altitude and evolution were unified in one graph. n.i., Not identified

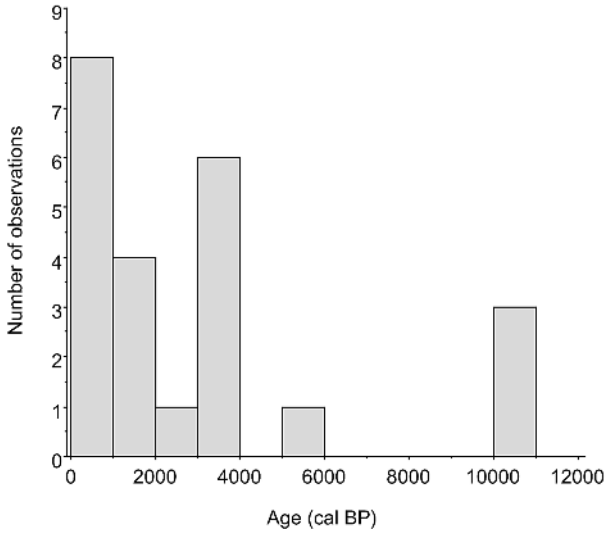

Figure 6 Distribution of the ^{14}C ages (number of observations) over the considered time span

and Thinon, 1996). As no big changes in vegetation have been recognised at our sites, we can assume that the area was dominated by mixed coniferous forests since the early Holocene and that the climate was relatively constant. The distinct warming of the climate after the Boreal chronozone (around 9000 years ago) gave rise to a rapid melting of the glaciers and enabled the Mesolithic human settlements up to the main Alpine range (Bassetti and Angelucci, 2007). At the passage between Boreal and Atlantic (9000–7400 cal. BP) *P. sylvestris* and *P. mugo* started to decline and mixed stands *Larix/Picea* increased their presence (Pini, 2002; Piussi, 1992).

(2) Copper, Bronze and early Iron Age (4300–400 BC) (Figure 7b)

The Trentino region was at that time already populated, as documented by the finding of the Alpine 'iceman' dated to 5300–5050 cal. BP (Baroni and Orombelli, 1996). The period around 4000 cal. BP is considered to be the beginning of the integration of high-mountain pastures with hunting practices (Marzatico, 2007). A clear evidence of these practices is the presence of *Plantago lanceolata* pollens in Alpine peat bogs (Della Casa, 2001). The first human interference in the investigation area is recorded during the Copper Age, at around 3000 BC. The charcoal fragments extracted from the soil 'Cad' at an altitude of 1521 m a.s.l. with an age of 3378–3089 cal. BC could be due to human settlements in the sub-Alpine altitudinal range. Already in the late Neolithic the use of fire to open up new pastures has been documented (eg, Kaufmann and Demetz, 2004). Other studies in nearby Alpine and sub-Alpine sites in Trentino and in Austria reported an increase in agricultural and pastoral practices in valleys during that time (Cucina *et al*., 1999; Schmidl *et al*., 2005). The first clearances were carried out in deciduous forests of the valley bottoms and indicate the location of settlements in the surroundings. The occurrence of birch (*Betula* sp.), hornbeam (*Carpinus betulus*), pine (*Pinus*) and larch (*Larix*) shows an opening-up of the forests for timber, firewood and agricultural use. The beginning of the human activity is indicated by the first occurrence of ribwort plantain (*Plantago lanceolata* type) and juniper (*Juniperus communis*) (Schmidl *et al*., 2005), species common nowadays in the sub-Alpine and Alpine altitudinal range (Carnelli *et al*., 2004b).

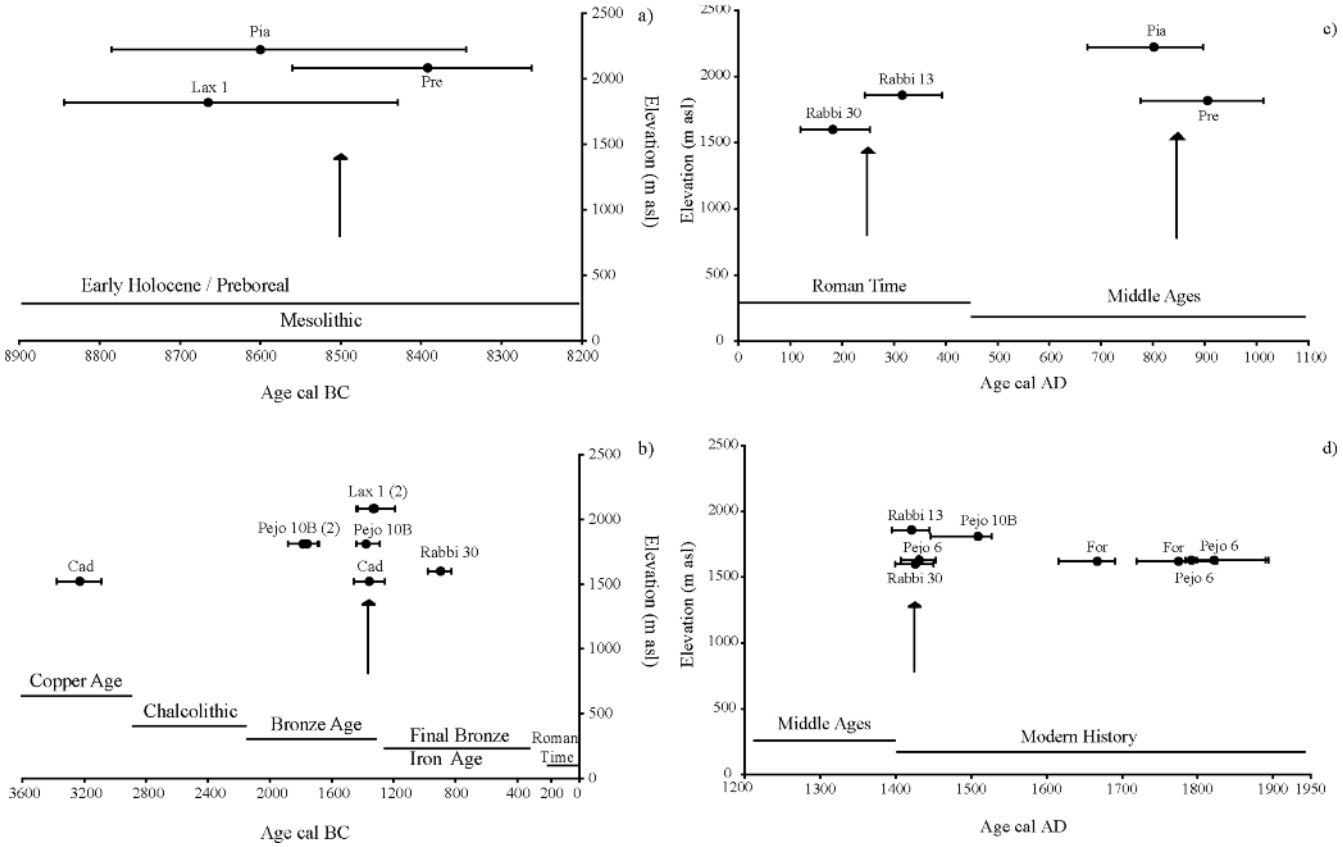

Figure 7 Chronology of fire events: (a) during the Mesolithic period, (b) until the late Iron Age, (c) during Roman time and early Middle Ages, (d) late Middle Ages and Modern history. The 1 σ range of the calibrated ^{14}C ages is given with the median value

In the Copper Age, Alpine passes were intensively used to transport merchandise (eg, painted pottery) to Middle Europe (Pedrotti and Demetz, 1997). Trading along commerce routes had been common since the Neolithic (5000–3200 cal. BC; Moe *et al*., 2007), mainly along the valleys. The fire reported during this period is probably of human origin, but more fragments are needed to confirm this hypothesis. *Larix* meadows (a form of grazed forest still present nowadays) started to spread around 4820 cal. BP, simultaneous with a phase of anthropic cutting of *Picea*. *Larix* pollens of this period represent the highest percentage (Pini, 2002). In the altitudinal range 1500–1800 m a.s.l. *P. abies* trees started to be present in combination with *Pinus* (Burga and Perret, 1998).

The charcoal fragments of 1400–1800 cal. BC (3350–3750 cal. BP; early and middle Bronze Age) correlate well with the climate change that occurred around 3000–3500 BP leading to the Göschener cold-phases (Zoller *et al*., 1966; Burga and Perret, 1998; Maisch *et al*., 1999). The treeline reached an altitude similar to the present (around 2100 m a.s.l.). In addition, human impact has increasingly influenced the treeline since that period (Di Benedetto *et al*., 2000; Schmidl *et al*., 2005). Compared with the Neolithic, later human impact on the landscape became more intense, with more extensive cultivation (Eckmeier *et al*., 2007) and animal husbandry, accompanied by a development towards more complex societies (Castelletti *et al*., 2001). The vegetation pattern of nearby sites in Trentino (Valsecchi *et al*., 2006) suggested that the landscape has been exposed to more intense human impact since about 2000 BC. The human presence in the Bronze Age is supported by several finds of artefacts in Alpine valleys in Austria, Germany and Trentino (Finsinger, 2001; Schmidl *et al*., 2005; Eckmeier *et al*., 2007). In our investigated sites, this period is represented by the charcoal layer found in 'Pejo 10B' at around 75 cm of soil depth and which is mainly composed of charcoal fragments of the Bronze Age and by three fires which occurred in the area between 1800 and 900 cal. BC (Table 3 and Figure 7b). The charcoal fragments dated back 1400 cal. BC demonstrated a synchronicity which could be due to climate forcing, as the soils are located between 1500 and 2100 m a.s.l. and on different sides of the investigated area (Figures 1 and 7b). This event could also be caused anthropogenically, since the human impact activity in that period was high (Brochier *et al*., 1998; Castelletti *et al*., 2001).

Isolated fires occurred between 1800 and 900 cal. BC (Table 3; Figure 7b). During the transition from the middle to the final Bronze Age (1300–800 cal. BC), a shift towards more intense grazing and to increased cereal cultivation was suggested by archaeological evidence and by palaeobotanical records of Pian di Gembro and Lago Lucone near the Garda Lake (Valsecchi *et al*., 2006). Charcoal of local origin and increased values of *Poaceae* and most herbs showed active grazing until about 2000 cal. BP (Moe *et al*., 2007). In that period, *Larix* meadows definitely took the place of former *Pinus* stands (Pini, 2002).

(3) Late Iron Age, Roman time and Middle Ages (400 BC–AD 1400) (Figure 7c)

Only few charcoal fragments were found that could be attributed to the Roman time period and the late Iron Age (*c*. 400 BC–AD 630). This suggests a decrease in the use of fire in land use (Galop *et al*., 2000). Such a reduction can be explained as the result of a more attractive economy in the lowlands and specialisation in viticulture (Riera-Mora and Esteban-Amat, 1994). Similar observations were made for the same period in western Germany and in Scotland (Clark *et al*., 1989; Edwards and Whittington, 2000). One natural fire can be recognised around 250 cal. AD in the eastern part of the investigated area (profiles 'Rabbi 30' and 'Rabbi 13') (Figures 1 and 7c). The synchronicity of the ^{14}C age of their charcoal fragments and their geographical position suggest the occurrence of a natural fire which affected both sides of Val di Rabbi (Figure 1). Around 800 cal. AD another fire was recorded in the western part of the investigated area (soils 'Pia' and 'Pre', Val di Pejo – Figure 1) at an elevation between 1800 and 2200 m a.s.l. In this period of the Middle Ages, an increase in agricultural activities was recorded in several mountainous slopes (eg, Galop, 1998; Galop *et al*., 2000) with the concomitant effect of regional fires. Palynological studies in lakes of Trentino (Filippi *et al*., 2005), Austria (Kral, 1971), France (Wegmüller, 1977) and Switzerland (Gobet *et al*., 2004) support an increase of the human impact in Alpine valleys as shown by the high deforestation rates and by the development of high-elevation pastures during the first period of the Middle Ages (600–1000 cal. AD). According to the possible land use of that time, we hypothesise the fires between 1800 and 2200 m a.s.l. to be caused by human activity such as the opening of new pastures.

(4) Modern history (> AD 1400) (Figure 7d)

According to the ^{14}C ages of the charcoal fragments, the greatest human impact in Modern history was recorded in the elevation range 1500–1800 m a.s.l. (Figure 7d, Table 3). The existence of several iron-smelting sites in Val di Sole (Speranza *et al*., 1996) could explain the need for wood. A synchronous fire was recorded in the western and eastern part of the investigated area at around 1420 cal. AD. Studies from the Pyrenees indicated an extensive human pressure on the landscape during the last centuries (Galop *et al*., 2000). At the end of the nineteenth century, the pastures reached their maximum extent until the latest period of the twentieth century which was characterised by a great increase in forest regeneration and expansion because of the countryside being abandoned and the progressive industrialisation of the region (Filippi *et al*., 2005). The high presence of more recent charcoal fragments suggests an increase in the use of fire for pasture management or for charcoal production (charcoal piles). The soil at the site 'For' is a typical example of this practice in recent centuries. The first 25 cm of this soil were almost entirely composed of charcoal fragments, most of them having a diameter of > 2 cm. The C stock was almost entirely composed by charcoal fragments (Table 2, Figure 8). The dated charcoal fragments of this soil all had a similar age (1700 cal. AD and younger). The western part of the investigated area (Val di Pejo) was probably utilised for relatively intense agro-forestry activities, as demonstrated by the five fires which occurred during the last 500 years (Figure 7d). This valley is still relatively intensively used today.

Soil evolution

The most developed soils in the siliceous Alpine environment are usually podzols, whose degree of evolution can be used to estimate the stability of surfaces (Egli *et al*., 2003; Briggs *et al*., 2006). In the case of undisturbed soil development, the age of the

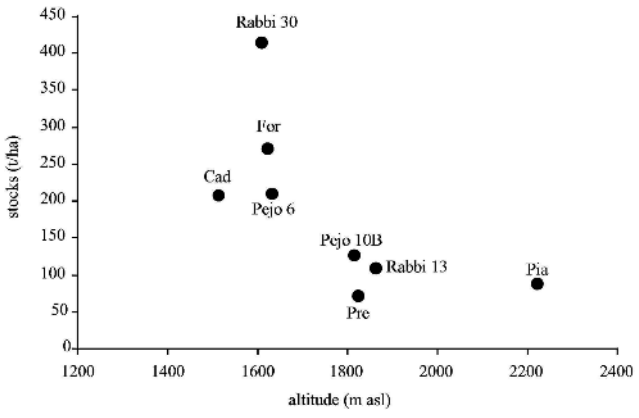

Figure 8 Abundance of organic carbon (kg/m^2) in the soils as a function of the altitude

oldest charcoal fragments can be directly linked to soil age (see Favilli *et al*., 2008). Charcoal fragment in soils can help to estimate soil age (Carcaillet, 2001). The soils 'Pre', 'Lax 1' and 'Pia' have charcoal fragments that can be related to the beginning of the Holocene (10 200–10 700 cal. BP; Table 3) and consequently can give an indication about the soil formation. According to the ^{14}C age of the charcoal and to the development of the horizons, an undisturbed soil evolution has been taking place during the last 10 000 years on stable surfaces of higher elevation. Such a time span leads to well-developed podzols (Lundström *et al*., 2000; Sauer *et al*., 2007). Sites with repeated fire events or a high charcoal content (such as 'For' or 'Cad') may be subjected to soil degradation and erosion: the site 'For' had a relatively shallow soil. It has been shown that post-fire flow erosion rates exceed long-term rates up to a factor of six (Roering and Gerber, 2005). Given the sensitivity of steep hillslopes to post-fire-driven transport, changes in climate and fire frequency may affect soil resources by disturbing the balance between soil transport and production.

In Alpine environments, the stocks of organic C close to the treeline are considerable (> 230 t/ha, up to 400t/ha; Hitz *et al*., 2002; Tonolli and Salvagni, 2007). The abundance of soil organic carbon (SOC) usually shows a non-linear climate dependent tendency (Egli *et al*., 2006). Highest amounts of SOC are measured in the sub-Alpine range or near the treeline. In this range, a high amount of flammable wood can be provided and the probability of fires due to lightening is increased (Figure 8).

The measured charcoal stocks in the soils (Cad, Pre and Pia: 1.3–8.8 t/ha, Table 2) correspond approximately to values recorded in the southern Alps (Schlumpf, 2004) where forest fires are frequent. The amount of charcoal measured at the site 'For' was 247.5 t/ha, which makes it almost the sole contributor to the total soil organic carbon. This site definitely must have been affected by a charcoal pile.

Conclusions

We used the age of 23 charcoal fragments extracted from nine sub-Alpine and Alpine soils in Val di Sole to reconstruct the landscape evolution since the beginning of the Holocene and to separate, as far as possible, naturally driven from human-induced processes. We obtained the following findings:

(1) Sub-Alpine and Alpine soils are good archives about past climatic evolution and human impact on landscape evolution.

(2) The signal of the charcoals in the soils agreed well over the last 10 000 years with existing archaeological and botanical proxies (ie, palynological).

(3) Synchronous charcoal fragments at different sites are possible evidence for natural fires which occurred in several parts of the region, mainly induced by climatic conditions (ie, dry periods, lightning).

(4) Isolated fires are probably human-induced but more charcoal fragments of the same age in the same site are needed to support such a hypothesis.

(5) The charcoal chronology shows at least 13 fire events in the last 10 000 years, of which seven or eight are likely to be human-induced.

(6) A quick forest expansion phase must have occurred shortly after the Lateglacial around 10 500 cal. BP. *Pinus sylvestris* and *Pinus mugo*, as well as *Larix decidua,* populated the investigation area in that period. At the transition to the Boreal, *Picea abies* had not yet settled into this region.

(7) *Pinus sylvestris* and *Pinus mugo* were displaced around 4000 cal. BP.

(8) At the beginning of the Holocene the treeline was at a higher altitude compared with the present-day but was heavily influenced by human activities during the centuries.

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Part C
Appendix

Table 1
Characteristics of the investigated soils

Soil profile	Elevation (m asl)	Aspect (°N)	Slope (%)	Parent material	Vegetation	Land use	WRB (IUSS 2006)
Cad	1521	275	18	Micaschists	*Larix decidua / Picea abies*	Natural forest	Entic Podzol
Rabbi 30	1600	25	43	Paragneiss	*Larix decidua / Picea abies*	Natural forest	Entic Podzol (Endoskeletic).
For	1621	350	12	Micaschists	*Larix decidua / Picea abies*	Natural forest	Cambic Umbrisol
Pejo 6	1630	120	70	Micaschists	*Larix decidua / Picea abies*	Natural forest	Cambic Umbrisol
Pejo 10B	1810	130	70	Micaschists	*Larix decidua / Picea abies*	Natural forest	Haplic Cambisol (Dystric)
Pre	1818	305	5	Micaschists	*Larix decidua*	Natural forest	Entic Podzol
Rabbi 13	1860	185	65	Micaschists	*Picea abies / Larix decidua*	Natural forest	Haplic Cambisol (Dystric)
S6	2076	5	38	Paragneiss	*Larix decidua / Juniperus communis*	Natural forest	Entic Podzol
S5 (Lax 1)	2083	240	32	Paragneiss	*Larix decidua / Juniperus communis*	Natural forest	Entic Podzol
S1 (Rabbi 38)	2100	60	32	Paragneiss	*Larix decidua / Juniperus cimmunis*	Natural forest	Entic Podzol
S7	2100	3	43	Paragneiss	*Larix decidua / Juniperus communis*	Natural forest	Umbric Podzol
Pia	2222	350	21	Micaschists	*Rhododendro – vaccinietum extrasilvaticum*	Natural grassland and shrubs	Haplic Cambisol (Dystric)
S2	2230	70	55	Paragneiss	*Rhododendro – vaccinietum extrasilvaticum*	Natural grassland	Haplic Podzol
S4	2370	300	10	Paragneiss	*Festucetum*	Natural grassland	Brunic Regosol
S3	2380	320	5	Paragneiss	*Festucetum*	Natural grassland	Protospodic Leptosol

S9	2449	90	0	Paragneiss	*Carex curvula / Nardus stricta*	Natural grassland	Umbric Podzol
S8	2552	200	33	Paragneiss	*Carex curvula / Nardus stricta*	Natural grassland	Cambic Umbrisol

Table 2. List of samples, elevation, latitude of the sample sites, thickness of sample, correction factor for topography, snow, ^{10}Be measured concentration in the sample, measurement error and ^{10}Be date.

Sample	Elevation (m asl)	Latitude (°N)	Lithology / Location	Sample thickness (cm)	Shield correction	Snow correction (meters)*	^{10}Be (at g^{-1} 1E+5])	Estimated total error** (%)	^{10}Be date (yr)	^{10}Be date (snow corrected) (yr)
B1	2247	46.2263	Gneiss / lateral moraine	3	0.931	1.3	3.23 ± 0.21	10.2	11680 ± 1180	13240 ± 1350
B2	2360	46.2223	Gneiss / moraine crest	5	0.927	0.7	3.25 ± 0.15	8.5	11110 ± 940	11890 ± 1010
B3	2456	46.2223	Gneiss / lateral moraine	5	0.958	0.3	3.15 ± 0.18	7.8	9780 ± 770	9940 ± 770
B4	2446	46.2223	Gneiss / lateral moraine	5	0.959	0.3	2.86 ± 0.19	7.8	8710 ± 680	8850 ± 690
B5	2360	46.2223	Gneiss / lateral moraine	5	0.797	0.7	2.31 ± 0.11	11.8	9190 ± 1090	9840 ± 1160
B6	2552	46.2315	Gneiss / rock glacier	4	0.978	0.5	3.01 ± 0.13	9.6	8720 ± 840	8960 ± 860
B7	2449	46.2302	Gneiss / moraine ridge	5	-	-	-	-	n.d.	n.d.
B8	2597	46.2308	Micaschists / transfluence pass	5	0.986	0.5	4.16 ± 0.20	9.2	11490 ± 1060	12040 ± 1110
B9	2586	46.2308	Micaschists / transfluence pass	5	0.956	0.5	3.84 ± 0.17	7.0	11030 ± 770	11550 ± 810
B10	2453	46.2160	Micaschists / ridge line	5	0.973	0.7	4.22 ± 0.15	5.7	12950 ± 740	13850 ± 790

n.d. = not determined

* average value of snow cover during 6 months

**estimated total error including measurement error and the effects of altitude, latitude and topography/depth scaling

Table 3a
Physical characteristics of the investigated soils (Manuscripts I, II, III)

Site	Soil horizon	Depth (cm)	Munsell colour (moist)	Skeleton[1)] (%)	Sand[2)] (g/kg)	***Silt*** (g/kg)	Clay (g/kg)
S1 (Rabbi 38)							
	AE	0-4	10YR 3/3	5	455	280	265
	BE	4-8	5YR 4/4	11	515	280	205
	Bs1	8-20	7.5YR 4/4	51	575	286	139
	Bs2	20-45	10YR 4/4	45	671	275	54
	BC	45-60	10YR 5/4	34	n.d.	n.d.	n.d.
S2							
	AE	0-9	7.5YR 2/1	3	397	398	205
	Bhs	9-20	7.5YR 3/3	19	717	209	74
	Bs	20-40	7.5YR 4/3	58	709	252	39
S3							
	AE1	0-4	10YR 2/3	8	457	223	320
	AE2	4-12	10YR 3/2	21	576	212	212
	Bhs	12-20	10YR 4/2	45	638	172	190
S4							
	A	0-8	10YR 3/2	0	352	496	152
	Bw1	8-20	10YR 4/4	1	409	437	154
	Bw2	20-32	10YR 4/4	32	692	258	50
	Ab	32-35	10YR 3/3	2	309	498	193
	Bb	35-40	10YR 4/4	49	839	136	25
S5 (Lax 1)							
	AE	0-11	10YR 4/3	7	437	302	261
	Bs1	11-26	5YR 4/6	16	551	344	105
	Bs2	26-50	7.5YR 4/6	47	663	258	79
S6							
	AE	8-17	2.5YR 5/1	54	438	417	145
	Bs1	17-38	5YR 4/6	67	561	317	122
	Bs2	38-45	7.5YR 4/6	68	561	317	122
	BC	45-60	10YR 4/6	56	530	353	117
S7							
	AE	5-10	10YR 2/1	43	498	290	212
	Bs1	11-25	10YR 3/3	63	544	323	133
	Bs2	25-50	10YR 3/3	44	536	331	133
	BC	50-60	10YR 3/3	60	532	333	135
S8							
	AE	0-20	7.5YR 3/2	37	486	374	140
	Bs	20-25	5YR 2/4	59	599	360	41
	BC	25-48	10YR 4/6	54	632	345	23
S9							
	AE	0-11	7.5YR 3/2	16	381	416	203
	Bs	11-23	7.5YR 3/3	27	497	400	103
	BC	23-40	7.5YR 4/4	46	654	310	36

[1)] Skeleton = Material > 2mm
[2)] Size fractions: sand = 2000−62µm, silt = 62−2µm, clay = <2 µm (n.d. = Not determined)

Table 3b
Physical characteristics of the investigated soils (Manuscript IV)

Site	Soil horizon	Depth (cm)	Munsell colour (moist)	Skeleton[1)] (%)
Cad				
	O	0-12	7.5YR 3/3	3
	AE	12-20	7.5YR 3/4	3
	BA	20-35	7.5YR 4/6	15
	Bs1	35-45	10YR 4/6	15
	Bs2	45-70	7.5YR 5/6	35
Rabbi 30				
	AE	18-25	10YR 1.7/1	30
	Bs1	25-50	7.5YR 4/3	50
	Bs2	50-60	5YR 3/3	60
	BC	60-90	10YR 4/6	70
For				
	OE	0-25	10YR 1.7/1	0.5
	Bs	25-50	7.5YR 4/6	5
Pejo 6				
	AE	0-10	7.5YR 3/2	10
	BA	10-35	7.5YR 3/2	15
	Bs	35-58	7.5YR 4/4	15
	BC	58-85	10YR 4/4	35
Pejo 10B				
	A	4-10	7.5YR 3/2	10
	Bs1	10-50	7.5YR 4/3	30
	Bs2	50-70	5YR 3/2	50
	BC	70-80	10YR 4/4	60
Pre				
	A	0-3	10YR 3/2	1
	AE	3-12	10YR 4/4	20
	Bs	12-45	10YR 5/4	20
	BC	45-60	10YR 4/6	15
Rabbi 13				
	AB	3-10	10YR 4/4	10
	Bs1	10-37	7.5YR 4/6	15
	Bs2	37-55	7.5YR 4/6	25
	BC	55-100	2.5YR 5/4	45
Pia				
	AE1	0-8	7.5YR 3/2	3
	AE2	8-11	7.5YR 4/3	10
	BE	11-25	7.5YR 4/4	20
	Bs1	25-55	7.5YR 4/6	40
	Bs2	55-80	10YR 4/6	40

[1)] Skeleton = Material > 2mm

Table 4
Chemical characterisation of the investigated soils

Site	Soil horizon	pH ($CaCl_2$)	Org. C (g/kg)	Total N (g/kg)	C/N	Fe_t (g/kg)	Si_o (g/kg)	Al_o (g/kg)	Fe_o (g/kg)	Fe_d (g/kg)	Al_d (g/kg)	$Al_o + 0.5\ Fe_o$ (%)
S1 (Rabbi 38)												
	AE	3.7	103.7	5.7	18	27.12	0.01	1.73	5.57	15.90	2.50	0.45
	BE	3.6	61.0	2.9	21	33.63	0.01	1.91	6.06	20.50	2.80	0.49
	Bs1	4.1	39.4	1.8	22	62.44	0.00	10.27	19.62	44.10	14.70	2.01
	Bs2	4.4	17.0	0.7	24	52.50	0.00	5.84	9.37	21.40	7.30	1.05
	BC	4.5	7.5	0.6	12	49.28	0.94	4.04	1.67	6.90	5.60	0.48
S2												
	AE	3.4	184.6	28.1	7	27.69	0.00	2.78	5.67	14.53	3.94	0.56
	Bhs	3.7	63.8	11.8	5	65.10	0.07	6.31	24.90	45.33	5.96	1.88
	Bs	4.1	25.4	8.8	3	64.46	0.47	6.41	8.81	30.13	10.65	1.08
S3												
	AE1	3.4	124.9	6.8	18	17.41	0.09	2.03	2.47	8.50	2.80	0.33
	AE2	3.5	48.0	2.2	22	26.80	0.12	2.48	4.33	11.00	3.20	0.46
	Bhs	3.8	71.4	3.1	23	46.36	0.00	8.30	13.76	27.10	14.20	1.52
S4												
	A	3.8	55.3	3.8	15	59.60	0.21	3.05	7.05	21.90	5.40	0.66
	Bw1	4.0	20.7	1.5	14	69.31	0.19	2.47	9.61	30.80	5.00	0.73
	Bw2	4.1	19.5	1.3	15	60.37	0.13	1.58	4.21	20.60	3.30	0.37
	Ab	3.9	62.0	3.9	16	48.38	0.17	4.39	6.52	23.10	7.50	0.76
	Bb	4.2	9.1	0.5	18	56.16	0.09	1.57	3.70	15.30	2.70	0.34
S5 (Lax 1)												
	AE	3.5	56.9	2.7	21	35.31	0.05	2.18	7.13	21.10	3.10	0.57
	Bs1	3.8	35.3	1.7	21	69.36	0.12	6.42	20.19	50.70	9.50	1.65
	Bs2	4.3	22.8	1.1	21	56.78	0.36	6.35	10.08	24.50	8.60	1.14
S6												
	AE	3.5	76.5	4.1	19	24.64	0.022	1.49	3.88	13.54	1.82	0.34
	Bs1	4.0	45.3	1.8	25	55.7	0.089	5.60	16.46	35.81	8.21	1.38
	Bs2	4.1	47.6	1.6	30	-	0.124	5.53	15.57	35.18	9.20	1.33
	BC	4.2	35.5	1.1	32	44.24	0.115	4.09	14.42	30.47	6.57	1.13
S7												
	AE	3.1	143.9	6.4	22	21.62	0.063	0.89	1.52	8.06	1.33	0.16
	Bs1	3.7	48.5	1.4	35	24.3	0.050	1.92	4.39	12.64	3.26	0.41
	Bs2	3.7	48.3	1.6	30	-	0.012	1.81	3.54	10.43	2.89	0.36
	BC	3.7	48.7	1.5	32	22.7	0.036	1.90	3.64	11.12	3.23	0.37
S8												
	AE	3.8	43.0	2.3	19	31.92	0.87	4.63	6.18	22.82	7.82	0.77
	Bs	4.2	29.5	1.4	21	-	2.51	6.21	6.32	19.09	8.69	0.94
	BC	4.4	8.0	0.5	16	32.97	5.75	3.30	1.97	13.92	4.40	0.43
S9												
	AE	3.2	56.4	3.8	15	18.6	0.07	3.15	4.60	12.65	3.04	0.55
	Bs	3.8	37.8	1.6	24	-	0.98	7.32	10.74	31.06	8.30	1.27
	BC	4.1	17.9	0.7	26	41.02	1.42	4.08	4.01	18.64	5.91	0.61
Cad												
	O	4.2	161.9	10.4	15	-	-	-	-	-	-	-
	AE	4.0	55.5	3.5	15	-	-	1.41	4.85	-	-	0.38
	BA	4.1	30.4	1.7	18	-	-	4.27	7.68	-	-	0.81
	Bs1	4.2	16.5	0.9	17	-	-	2.26	2.63	-	-	0.36

	Bs2	4.3	17.2	0.9	19	-	-	1.24	2.46	-	-	0.24
Rabbi 30												
	AE	3.0	103.5	5.0	21	-	-	3.66	3.36	-	-	0.53
	Bs1	3.4	59.0	2.6	23	-	-	5.21	10.52	-	-	1.05
	Bs2	3.7	87.3	3.9	22	-	-	10.35	18.22	-	-	1.95
	BC	3.9	63.1	2.2	29	-	-	10.10	15.61	-	-	1.79
For												
	OE	3.9	137.6	4.1	34	-	-	3.02	5.06	-	-	0.55
	Bs	4.2	25.7	1.2	21	-	-	4.37	6.85	-	-	0.78
Pejo 6												
	AE	3.8	115.1	6.2	19	-	-	2.02	5.41	-	-	0.47
	BA	4.0	36.3	13.3	3	-	-	3.9	7.37	-	-	0.76
	Bs	4.6	12.4	1.2	10	-	-	3.62	4.83	-	-	0.61
	BC	4.7	7.6	0.6	11	-	-	1.62	4.45	-	-	0.38
Pejo 10B												
	A	3.9	46.8	2.4	19	-	-	2.37	6.17	-	-	0.55
	Bs1	4.0	14.6	0.6	24	-	-	2.71	6.53	-	-	0.59
	Bs2	4.3	16.1	0.6	27	-	-	3.09	7.62	-	-	0.69
	BC	4.3	72.3	2.0	36	-	-	7.06	10.77	-	-	1.24
Pre												
	A	3.9	62.4	3.6	17	-	-	1.61	5.11	-	-	0.42
	AE	4.1	30.6	1.8	17	-	-	1.83	5.46	-	-	0.46
	Bs	4.7	17.8	1.2	17	-	-	6.98	9.15	-	-	1.15
	BC	4.8	7.5	0.5	14	-	-	3.20	4.31	-	-	0.23
Rabbi 13												
	AB	4.2	24.4	0.6	40	-	-	2.15	4.66	-	-	0.45
	Bs1	4.3	20.2	0.8	25	-	-	2.68	4.44	-	-	0.49
	Bs2	4.9	10.3	0.7	15	-	-	4.47	4.88	-	-	0.69
	BC	5.0	4.3	0.4	11	-	-	2.08	1.05	-	-	0.26
Pia												
	AE1	4.6	75.8	4.4	17	-	-	-	-	-	-	-
	AE2	4.4	52.4	3.3	16	-	-	1.49	5.04	-	-	0.41
	BE	4.3	14.4	0.9	15	-	-	1.38	5.05	-	-	0.39
	Bs1	4.5	8.7	0.6	14	-	-	1.87	5.46	-	-	0.46
	Bs2	4.7	7.1	0.5	15	-	-	1.66	4.48	-	-	0.39

- = Not determined

t = Total content; o = Oxalate extractable content; d = Dithionite extractable content

Table 5a Measured and calibrated radiocarbon ages of untreated and H_2O_2-treated soil samples. Calibrated ^{14}C ages are given in the 2 σ range. (Manuscripts I, II, III)

Site	Soil Type depth (cm)	Soil horizon	Uncal ^{14}C untreated	Cal ^{14}C untreated	ETH Numbers H_2O_2-treated	Uncal ^{14}C H_2O_2-treated	Cal ^{14}C H_2O_2-treated
S1	Entic Podzol						
(Rabbi 38)							
	0-4	AE	-650 ± 40	Modern	ETH-33508	12470 ± 90	14160 – 14964
	4-8	BE	-30 ± 40	Modern	ETH-33509	14410 ± 110	16782 – 17839
	8-20	Bs1	780 ± 40	666 – 772	ETH-33510	10060 ± 85	11274 – 11972
	20-45	Bs2	2815 ± 45	2794 –3064	ETH-33511	9735 ± 75	10786 – 11270
	45-60	BC	-	-	-	-	-
S2	Haplic Podzol						
	0-9	AE	-	-	ETH-33972	2360 ± 50	2207 – 2699
	9-20	Bhs	-	-	-	-	
	20-40	Bs	-	-	ETH-33973	9775 ± 70	10825 – 11386
S3	Protospodic Leptosol						
	0-4	AE1	-	-	ETH-33976	5115 ± 55	5729 – 5989
	4-12	AE2	-	-	-	-	
	12-20	Bhs	650 ± 50	546 – 676	ETH-33977	9425 ± 75	10435 – 11073
S4	Brunic Regosol						
	0-8	A	-	-	ETH-33974	7655 ± 65	8370 – 8585
	8-20	Bw1	-	-	-	-	-
	20-32	Bw2	-	-	ETH-35573	8025 ± 60	8647 – 9073
	32-35	Ab	2505 ± 50	2366 – 2743	ETH-33975	11920 ± 85	13596 – 13991
	35-40	Bbw	-	-	-	-	-
S5	Entic Podzol						
(Lax 1)							
	0-11	AE	85 ± 50	10 – 237	ETH-33512	9495 ± 75	10575 – 11099
	11-26	Bs1	570 ± 50	518 – 654	ETH-33513	8125 ± 70	8788 – 9294
	26-50	Bs2	1525 ± 50	1318 – 1525	ETH-33514	7700 ± 75	8377 – 8627
S6	Entic Podzol						
	8-17	AE	-	-	ETH-35565	2825 ± 50	2792 – 3076
	17-38	Bs1	-	-	-	-	-
	38-45	Bs2	-	-	ETH-35566	4235 ± 50	4583 – 4874
	45-60	BC	-	-	-	-	-
S7	Umbric Podzol						
	5-10	AE	-	-	ETH-35563	2880 ± 50	2870 – 3202
	11-25	Bs1	-	-	-	-	-
	25-50	Bs2	-	-	ETH-35564	4710 ± 50	5320 – 5584
	50-60	BC	-	-	-	-	-

S8	Cambic Umbrisol						
	0-20	AE	-	-	ETH-35567	8195 ± 60	9009 – 9397
	20-25	Bs	-	-	-	-	-
	25-48	BC	-	-	ETH-35568	6445 ± 55	7271 – 7433
S9	Umbric Podzol						
	0-11	AE	-	-	ETH-35383	9795 ± 85	10794 – 11600
	11-23	Bs	-	-	-	-	-
	23-40	BC	-	-	ETH-35384	7200 ± 70	7875 – 8175

- = not determined

Table 5b Measured and calibrated radiocarbon ages of charcoal fragments > 2mm. Calibrated ^{14}C ages are given in the 2 σ range. (Manuscript IV)

Site	Soil horizon	Depth (cm)	Charcoal fragment	Macrocharcoal g/kg soil	Uncal ^{14}C	Cal ^{14}C BP	Calendar age (years BC/AD) and prehistoric civilization
Cad							
	O	0-12	-				
	AE	12-20	-				
	BA	20-35	-				
	Bs1	35-45	Clematis	0.3	3090 ± 50	3205 – 3405	1456 – 1256 BC Bronze Age
	Bs2	45-70	Ericaceae	0.1	4550 ± 55	5038 – 5327	3378 – 3089 BC Copper Age
Rabbi 30							
	AE	18-25	Larix decidua	3.3	495 ± 30	500 – 551	1399 – 1450 AD Modern
	Bs1	25-50	Larix decidua	0.3	1830 ± 30	1698 – 1831	119 – 253 AD Roman Empire
	Bs2	50-60	Larix decidua	0.1	2755 ± 35	2774 – 2929	825 – 980 BC Bronze Age
	BC	60-90	-				
For							
	OE	0-25	Larix decidua	89.3	240 ± 45	260 – 334	1616 – 1691 AD Modern
			Larix decidua		185 ± 45	124 – 231	1719 – 1826 AD Modern
	Bs	25-50	-				
Pejo 6							
	AE	0-10	Larix decidua	2.2	130 ± 30	57 – 152	1799 – 1894 AD Modern
	BA	10-35	Larix decidua	0.7	150 ± 30	167 – 233	1718 – 1734 AD Modern
	Bs	35-58	Larix decidua	0.7	480 ± 30	498 – 543	1407 – 1453 AD Modern
	BC	58-85	-				
Pejo 10B							
	A	4-10	Larix decidua	3.1	375 ± 30	424 – 505	1446 – 1527 AD Modern
	Bs1	10-50	Ericaceae	0.3	3100 ± 35	3239 – 3390	1441 – 1290 BC Bronze Age
	Bs2	50-70	-				
	BC	70-80	Larix/Picea		3460 ± 35	3640 – 3831	1882 – 1691 BC Bronze Age
			Larix/Picea	9.7	3445 ± 35	3631 – 3832	1883 – 1682 BC Bronze Age
Pre							
	A	0-3	-				
	AE	3-12	Picea/Larix	0.2	1135 ± 50	937 – 1174	776 – 1031 AD Middle Age
	Bs	12-45	-				
	BC	45-60	Pinus sylvestris	0.1	9385 ± 75	10378 – 10793	8844 – 8429 BC Holocene
Rabbi 13							
	AB	3-10	Larix decidua	0.4	510 ± 30	505 – 555	1395 – 1445 AD Modern
	Bs1	10-37	Larix decidua	0.1	1725 ± 30	1557 – 1708	243 – 393 AD Roman Empire
	Bs2	37-55	-				
	BC	55-100	-				
Lax 1							
	AE	5-11	Larix/Picea	n.d.	3055 ± 50	3081 – 3381	1432 – 1192 BC Bronze Age
	Bs1	11-26	Larix/Picea	n.d.	3065 ± 55	3080 – 3393	1444 – 1191 BC Bronze Age

	Bs2	26-50	Larix/Picea	n.d.	9160 ± 70	10212 – 10509	8560 – 8263 BC Holocene
Pia							
	AE1	0-8	-				
	AE2	8-11	-				
	BE	11-25	Pinus/Larix	0.1	1220 ± 50	1054 – 1277	674 – 897 AD Middle Age
	Bs1	25-55	-				
	Bs2	55-80	Pinus sylvestris	0.1	9340 ± 75	10293 – 10734	8785 – 8344 BC Holocene

- = no charcoal fragments / size < 1 mm
n.d. = Not determined

Table 6
Minerals in the clay fraction of the investigated soil horizons: an overview (Manuscript III)

Site	Soil horizon	Smec[a]	Verm[a]	Mica/smec	mica/HIV	HIV[a]	Chlorite	Mica	Kaolinite
S1	AE	++	+	+	+	(+)	-	++	+
	BE	+	+	++	-	+	-	++	+
	Bs1	+	+	+	+	+	+	++	+
	Bs2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	BC	-	+	-	++	(+)	+	++	(+)
S2	AE	+	++	++	-	+	-	+	+
	Bhs	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Bs	-	+	-	++	+	(+)	+	+
S3	AE1	++	+	++	++	+	-	+	+
	AE2	+	++	-	-	-	-	++	+
	Bhs	+	-	++	+	(+)	+	++	+
S4	A	-	+	-	++	-	+	++	+
	Bw1	-	+	-	-	-	+	++	++
	Bw2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Ab	++	++	-	-	-	+	++	+
	Bb	-	+	-	-	+	+	++	++
S5	AE	+	(+)	++	+	+	-	++	+
	Bs1	++	+	+	+	+	+	++	+
	Bs2	+	+	++	++	-	+	++	+
S6	AE	++	(+)	++	-	+	(+)	++	+
	Bs1	+	+	++	+	(+)	+	++	+
	Bs2	+	+	++	+	+	+	++	+
	BC	-	++	-	+	+	+	+	+
S7	AE	++	(+)	++	+	+	-	++	+
	Bs1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Bs2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	BC	+	+	+	++	+	-	++	+
S8	AE	(+)	++	-	-	++	+	+	+
	Bs	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	BC	-	++	-	+	(+)	+	++	+

S9	AE	(+)	++	-	-	-	-	++	+
	Bs	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	BC	-	+	-	++	+	+	++	+

n.d. = not determined
(+) = traces (0-5%)
+ = present in significant amount (5-20%)
++ = present in high amount (> 20%)
- = not present
[a] HIV = hydroxy-interlayered vermiculite; smec = smectite; verm = vermiculite

Table 7
Geochemical characteristics (total analysis of the bulk material including soil skeleton (>2 mm up to 200 mm) and fine earth (<2 mm)) of the investigated soils (Manuscript III)

Site and soil horizon	Depth (cm)	Org. Matter (%)[a]	CaO (%)	MgO (%)	K_2O (%)	Na_2O (%)	Al_2O_3 (%)	Fe_2O_3 (%)	SiO_2 (%)	MnO (%)	TiO_2
S1											
AE	0-4	17.63	0.53	0.89	3.10	1.33	14.26	3.73	51.5	0.06	0.97
BE	4-8	9.23	0.43	0.93	3.40	1.35	15.74	4.77	57.2	0.07	1.03
Bs1	8-20	3.27	0.48	1.57	3.25	1.49	15.26	7.65	52.2	0.08	0.84
Bs2	20-45	1.59	0.73	1.69	3.00	1.62	14.95	6.54	59.3	0.07	0.78
BC	45-60	0.85	0.47	2.18	3.78	1.50	16.40	6.35	58.3	0.07	0.84
S2											
AE	0-9	31.75	0.64	0.53	1.90	1.18	8.84	3.82	37.4	0.02	0.75
Bhs	9-20	8.84	0.78	1.23	2.66	1.36	12.84	9.03	44.3	0.05	0.99
Bs	20-40	1.85	1.40	2.12	2.78	1.84	14.46	8.03	57.5	0.08	0.81
S3											
AE1	0-4	19.54	0.34	0.53	2.70	1.40	11.27	2.29	48.5	0.03	0.70
AE2	4-12	6.43	0.51	0.78	3.36	1.52	13.91	3.52	60.3	0.06	0.78
Bhs	12-20	6.67	0.52	0.97	2.93	1.41	12.67	5.28	52.4	0.06	0.63
S4											
A	0-8	9.41	0.64	2.54	3.84	1.35	17.25	8.68	47.6	0.04	0.87
Bw1	8-20	3.53	0.68	2.85	4.13	1.18	18.39	10.16	49.5	0.04	0.90
Bw2	20-32	2.26	1.16	2.44	3.36	1.81	16.27	8.18	57.8	0.07	0.87
Ab	32-35	10.54	1.49	2.24	2.69	2.11	13.95	6.88	67.8	0.08	0.75
Bb	35-40	1.55	1.65	2.10	2.10	2.35	13.84	6.62	64.6	0.10	0.74
S5											
AE	0-11	9.01	0.38	0.91	3.32	1.28	15.92	5.11	54.4	0.06	1.02
Bs1	11-26	5.06	0.38	1.27	3.13	1.57	15.25	9.41	51.6	0.08	0.91
Bs2	26-50	2.05	0.53	1.56	3.37	1.42	15.72	6.86	58.2	0.07	0.79
S6											
AE	8-17	3.85	1.63	2.35	2.87	2.54	14.79	4.34	65.3	0.04	0.96
Bs1	17-38	1.69	1.06	3.24	3.44	2.00	15.32	6.60	63.4	0.06	0.89
BC	45-60	1.68	1.11	2.03	3.32	1.95	14.30	5.26	68.6	0.05	0.85
S7											
AE	5-10	8.64	0.61	2.43	4.27	1.70	16.30	4.26	59.5	0.05	0.90
Bs1	11-25	2.09	0.74	2.70	3.90	2.03	15.50	3.94	67.7	0.06	0.88

BC	50-60	2.15	0.51	2.22	3.97	1.79	15.28	3.80	66.6	0.06	0.85
S8											
AE	0-20	2.81	0.97	1.03	3.21	2.71	13.49	3.91	68.9	0.07	0.40
BC	25-48	0.43	1.50	1.58	3.41	2.55	13.87	4.14	72.0	0.09	0.43
S9											
AE	0-11	4.98	0.49	1.06	2.77	1.75	14.00	2.93	61.9	0.03	0.78
BC	23-40	1.10	1.99	3.09	2.86	2.27	14.26	5.67	65.6	0.10	0.62

[a] Organic matter = org. C (of the fine earth and skeleton) * 1.72

Table 8
Strain coefficient ($\varepsilon_{i,w}$) and open-system mass transport function (τ) for each element investigated with respect to the sites and soil depth (Manuscript III)

Site	Horizons	Depth (cm)	$\varepsilon_{i,w}$	Si	Al	Fe	Mn	Mg	Ca	Na	K
S1											
	AE	0-4	0.36	-0.24	-0.25	-0.49	-0.28	-0.65	-0.03	-0.23	-0.29
	BE	4-8	0.27	-0.20	-0.21	-0.38	-0.25	-0.65	-0.26	-0.26	-0.26
	Bs1	8-20	0.90	-0.11	-0.07	0.20	0.16	-0.28	0.02	-0.01	-0.14
	Bs2	20-45	0.31	0.10	-0.02	0.11	0.14	-0.16	0.68	0.17	-0.14
	BC	45-60	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S2											
	AE	0-9	0.66	-0.29	-0.33	-0.48	-0.71	-0.73	-0.50	-0.30	-0.25
	Bhs	9-20	0.15	-0.36	-0.27	-0.07	-0.47	-0.52	-0.54	-0.39	-0.21
	Bs	20-40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S3											
	AE1	0-4	0.24	-0.17	-0.20	-0.61	-0.54	-0.51	-0.41	-0.10	-0.17
	AE2	4-12	0.06	-0.07	-0.11	-0.46	-0.17	-0.35	-0.21	-0.13	-0.08
	Bhs	12-20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S4											
	A	0-8	0.26	-0.37	0.07	0.13	-0.64	0.04	-0.67	-0.51	0.57
	Bw1	8-20	0.20	-0.37	0.09	0.26	-0.63	0.11	-0.66	-0.59	0.62
	Bw2	20-32	0.49	-0.24	0.00	0.06	-0.36	-0.01	-0.40	-0.34	0.37
	Ab	32-35	0.63	0.03	-0.01	0.02	-0.19	0.05	-0.11	-0.12	0.26
	Bb	35-40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S5											
	AE	0-11	0.29	-0.27	-0.21	-0.42	-0.39	-0.54	-0.44	-0.30	-0.23
	Bs1	11-26	0.29	-0.23	-0.16	0.19	0.02	-0.29	-0.37	-0.04	-0.19
	Bs2	26-50	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S6											
	AE	8-17	0.21	-0.16	-0.09	-0.27	-0.18	0.02	0.29	0.15	-0.24
	Bs1	17-38	-0.12	-0.13	0.01	0.19	0.13	0.51	-0.10	-0.03	-0.02
	BC	45-60	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S7											
	AE	5-10	0.70	-0.15	0.01	0.06	-0.19	0.04	0.14	-0.10	0.02
	Bs1	11-25	0.51	-0.02	-0.02	0.00	-0.04	0.17	0.39	0.09	-0.06
	BC	50-60	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S8											
	AE	0-20	0.73	0.01	0.03	0.00	-0.19	-0.31	-0.32	0.12	-0.01
	BC	25-48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S9											

AE	0-11	1.21	-0.25	-0.22	-0.59	-0.77	-0.73	-0.80	-0.39	-0.23
BC	23-40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

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